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Methanol Production from Biomass

R.J. Philp
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METHANOL PRODUCTION FROM BIOMASS

by

R.J. Philp

NRCC No. 27143

August 1986

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ABSTRACT

Methanol, currently used as a solvent, chemical feedstock, and as a gasoline extender, is produced from synthesis gas (syngas), which is a mixture of CO and H_2. The syngas is usually generated from natural gas; however, coal and biomass have been considered as alternative feedstocks.

The technical and economic aspects of the production of methanol from biomass are considered in this report. Since gasification represents the area of greatest technical risk in the use of biomass, a mathematical simulation of the process was used to determine the methanol supply price for various gasifiers under development. Although this price is relatively insensitive to the type of gasifier employed, syngas processing downstream of the gasifier is cost effective and research and development should focus on maximizing syngas yield from the gasifier.

The cost of methanol from biomass is comparable with that from coal, but the reduced financial risks with the biomass make it the preferred feedstock. Biomass, however, cannot compete with natural gas. Since the methanol supply price is insensitive to the type of gasifier further work in this area will not cause a substantial reduction in this price. Biomass will be unable to compete with natural gas unless a substantial price differential develops in feedstock costs.

RÉSUMÉ

Le méthanol, qu'on utilise actuellement comme solvant, comme produit chimique de base et comme allongeur pour l'essence, est préparé à partir du gaz de synthèse qui est un mélange de CO et de H_2. Le gaz de synthèse est habituellement produit à partir du gaz naturel, mais on a aussi envisagé d'utiliser le charbon et la biomasse.

Le présent rapport traite des aspects techniques et économiques de la production du méthanol à partir de la biomasse. Comme la gazéification représente l'élément technique le plus critique de l'utilisation de la biomasse à cette fin, on a fait appel à une simulation mathématique du processus pour déterminer le prix d'offre du méthanol correspondant à divers gazogènes en cours de développement. Ce prix est relativement indépendant du genre de gazogène employé. Néanmoins, comme le traitement du gaz de synthèse en aval du gazogène est rentable, l'effort de recherche et développement devrait surtout porter sur la maximisation de la production du gaz de synthèse par le gazogène.

Le prix de revient du méthanol produit à partir de la biomasse est comparable à celui du méthanol produit à partir du charbon. L'utilisation de la biomasse est toutefois privilégiée par rapport à celle du charbon en raison du peu de risque qu'elle comporte au point de vue financier. Par contre, la biomasse ne saurait se comparer au gaz naturel. Comme le prix d'offre du méthanol est indépendant du genre de gazogène utilisé, on ne peut s'attendre à ce que la poursuite des travaux dans le domaine des gazogènes entraîne une réduction importante du prix. La biomasse n'entrera en concurrence avec le gaz naturel que si son prix devenait nettement avantageux par rapport aux autres produits de base.

METHANOL PRODUCTION FROM BIOMASS

R.J. Philp

1. INTRODUCTION

Methanol, also known as wood alcohol and wood spirit, was discovered by Robert Boyle in 1661 and first synthesized by Berthelot in the 1850s. From the middle of the 19th until the early 20th century it was produced commercially by the destructive distillation of wood, but in 1923 BASF in Germany began commercial high pressure synthesis using gases containing carbon monoxide and hydrogen, and catalysts. The technology, based on synthesis gas (syngas), has continued to evolve and has had a significant impact upon the scale and efficiency of the process.

By 1965 (Kirk and Othmer, 1978) a high pressure (25-35 MPa) plant was producing 225 to 450 t/d of methanol for 330 d/a. Syngas was produced by the reforming of natural gas and approximately 1300 m^3 was required per tonne of methanol. Low pressure (5-10 MPa) processes developed by ICI and LURGI during the 1960s and early 70s resulted in improvements in conversion efficiency, and by 1980 a low pressure plant was producing 1000 to 2000 t/d of methanol for 350 d/a and using only 890 m^3 of natural gas per tonne of methanol. By 1982 the low pressure process (thermal efficiency = 68%) had completely replaced the high pressure one (thermal efficiency = 47%) in the United States.

The world production of methanol in 1981 was approximately 9.1 Mt and the American production was 3.8 Mt (United Nations, 1983). During the period 1972 to 1981, over which time the low pressure process became dominant, the world production, shown in Table 1.1, increased by 22% while the North American production increased by 35%.

Methanol has traditionally been used as a solvent and as an intermediate in the production of a large number of chemical compounds, such as formaldehyde. However, it has recently been introduced as a fuel extender (e.g., OXINOL™) for internal combustion engines and it is possible to use neat methanol as a transportation fuel and as a peakshaving turbine fuel for electricity generation (Beenackers and Van Swaaij, 1983; McIntosh, 1978; Kirk and Othmer, 1978; Lippe, 1981; Perez-Blanco, 1982; Othmer, 1985). However, the use of methanol as a fuel extender has been limited due to distribution, environmental (vapour pressure and emissions), and potential corrosion problems (Aydemir, 1984; Espinola et al., 1984; Cantwell and Smith, 1984; Dutkiewicz, 1984).

Table 1.1. Methanol production (kt)[1]

Year	N.A.[2]	Europe	Asia	World
1972	2958	2105	1157	7482
1973	3230	2295	1308	8179
1974	3149	2459	1175	8210
1975	2380	1979	806	6612
1976	3111	2468	1064	8024
1977	3354	2425	983	8170
1978	3401	2332	1217	8393
1979	3958	2477	1311	9145
1980	3853	2331	1102	8795
1981	4449	2155	962	9147

[1] From United Nations (1983) and Corpus (1981).
[2] N.A.: North America (U.S., Canada, and Mexico).

Although natural gas is currently the dominant feedstock used in the production of the syngas for the production of methanol, it is possible to use other feedstocks such as coal and biomass. However, the complexity of the process increases with these feedstocks and hence the capital cost as well (Resource Planning Associates, 1982). A block diagram showing one sequence of processing steps required for these feedstocks is shown in Figure 1.1. This paper will concentrate on biomass rather than coal since it offers a number of advantages over the latter, one being the lower consumption of nonrenewable energy compared to the energy value of the methanol produced (Jack Faucett Associates and Battelle-Columbus Lab, 1982). Acid gas removal, sulphur recovery, and effluent treatment costs are also reduced due to the lower S, Cl, and N concentrations in the wood. It is also claimed that thermal efficiencies for the wood process can exceed those for coal (Graboski, 1982). Thermal efficiencies have also been discussed by Reed (1976) for coal gasification and are very dependent upon the product distribution.

A serious impediment to the development of a coal-to-methanol industry is the scale of the proposed coal plants, which can be up to 18 kt/d

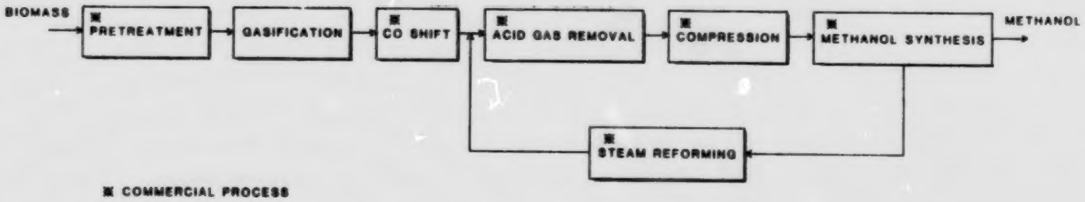


Figure 1.1. Methanol synthesis process sequence.

(Stratton et al., 1982), while current natural-gas-to-methanol plants consist of one or two trains of 1 kt/d. Substantial financial risks are involved and few corporations are prepared to invest in such projects without government assistance (Graboski, 1982). Also the time lag between the start of the project and revenue generation would incur substantial capital costs which would result in very high methanol selling prices, since over half of the annual operating costs are due to capital charges while approximately one quarter are due to feedstock costs (Resource Planning Associates, 1982). The methanol market could also be seriously disrupted as one of these plants came on-stream since its production could be one third to one half of the existing total methanol production. Finally, severe environmental and social impacts could occur in the localities where these plants would be situated.

By comparison, biomass or, specifically, wood plants would range in size from approximately 250 to 2000 t/d. Therefore, the financial hurdle would not be as great and the lag time could be reduced since components could be shop fabricated. Also, experience gained from the design and construction of the first plants could be more readily utilized for subsequent plants because of the size and time considerations. The effect of learning curve on cost reduction has been treated in greater detail by Summer et al. (1984). Plant size would also allow the product to be absorbed into local markets.

2. METHANOL SYNTHESIS

Methanol is formed from CO, CO_2, and H_2 as shown in the following reactions:

[1] $CO + 2H_2 = CH_3OH$ $\Delta H_{523} = -98.2$ kJ/mol

[2] $CO_2 + 3H_2 = CH_3OH + H_2O$ $\Delta H_{523} = -58.6$ kJ/mol

However, it is common practice to use reaction [1] and the inverse of the water gas shift reaction when describing the methanol synthesis equilibrium. The inverse water gas shift reaction is given in reaction [3].

[3] $CO_2 + H_2 = CO + H_2O$ $\Delta H_{523} = +39.7$ kJ/mol

The conversions of CO and CO_2 can be determined provided relationships are known for the equilibrium constants for equations [1] and [3] and the activity coefficients of the components (Kirk and Othmer, 1978). Equations for the equilibrium constants, as a function of the temperature, are given in equations [4] and [5] for reactions [1] and [3], respectively. It should be noted that the expression for K_1 cannot be taken as absolutely correct due to the variation in experimental results reported in the literature.

[4] $$K_1 = 9.74 \times 10^{-5} \times \exp(21.225 + 9143.6/T - 7.492 \ln T + 4.076 \times 10^{-3} \times T - 7.161 \times 10^{-8} \times T^2)$$

[5] $$K_3 = \exp(13.148 - 5639.5/T - 1.077 \ln T - 5.44 \times 10^{-4} \times T + 1.125 \times 10^{-7} \times T^2 + 49170/T^2)$$

where T is in Kelvin and K_1 is in $kPa^{-2}a$.

Equilibrium CO and CO_2 conversions are given in Tables 2.1 and 2.2 for various operating conditions and syngas compositions. Equations [4] and [5] have been used to estimate the values of the equilibrium constants and generalized correlations have been used for the activity coefficients (assuming ideal solution behaviour).

The temperature, pressure, and syngas composition have a significant effect on the CO and CO_2 conversions. In general the CO conversion is proportional to the pressure and the balance ratio and inversely proportional to the temperature. The balance ratio is a concentration ratio which is defined as $(H_2 - CO_2)/(CO + CO_2)$ (Van Dijk and Solbakken, 1984; Stratton et al., 1982; Hamilton, 1978; Rovner, 1983). Based on the stoichiometry of

Table 2.1. The effects of temperature and pressure on the equilibrium CO and CO_2 conversions for a syngas composition of 28% CO, 4% CO_2, and 68% H_2 (balance ratio = 2.0)

	CO conv., %		CO_2 conv., %		C conv. to methanol, %	
Temp., °C	Pressure, MPa 5	10	Pressure, MPa 5	10	Pressure, MPa 5	10
250	63.5	96.9	5.5	42.3	56.7	90.1
350	4.9	68	11.4	24.9	56.3	62.7

Table 2.2. The effects of temperature and pressure on the equilibrium CO and CO_2 conversions for a syngas composition of 58% CO, 4% CO_2, and 38% H_2 (balance ratio = 0.55)

	CO conv., %		CO_2 conv., %		C conv. to methanol, %	
Temp., °C	Pressure, MPa 5	10	Pressure, MPa 5	10	Pressure, MPa 5	10
250	20.3	31.4	0.6	0.3	19	29.4
350	1.8	22.2	3.2	2.8	1.9	20.9

reactions [1] and [3], the ideal concentration of H_2 in the syngas occurs when the balance ratio is two. As this ratio decreases the conversions of CO and CO_2 decrease.

In order to obtain a high carbon conversion, a portion of the product gas must be recycled to the inlet of the reactor. The recycle ratio (moles/moles) is dependent upon the syngas composition and the operating temperature and pressure. The effect of the balance ratio on the recycle ratio for various concentrations of CO_2 and CH_4 is shown in Figures 2.1 and 2.2, which have been generated using the simulation model described in Appendix A. Since CH_4 is neither a reactant nor a product in reactions [1] and [3] it behaves as an inert. This also applies to other syngas components such as N_2. The reactor temperature and pressure are 250°C and 5 MPa, and the concentration of inerts in the recycle has been arbitrarily set at 7.5%. For these operating conditions there exists a balance ratio which will minimize the recycle ratio. However, the minimum is also dependent upon the concentration of CO_2 and inerts in the syngas. It increases

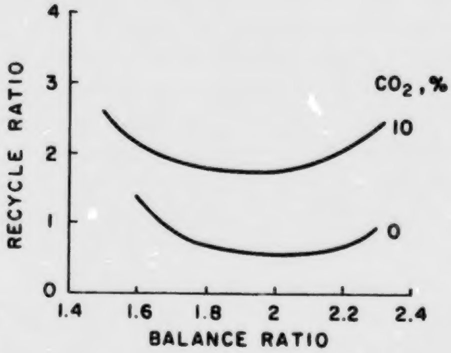


Figure 2.1. Effect of balance ratio and CO_2 concentration on recycle ratio. Concentration of CH_4 is 1%.

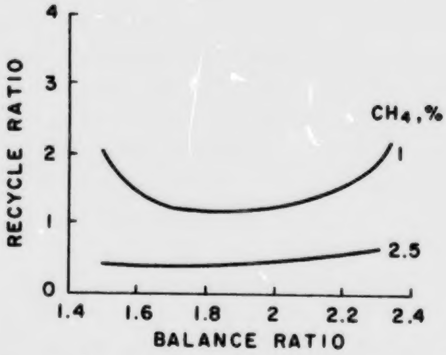


Figure 2.2. Effect of balance ratio and CH_4 concentration on recycle ratio. Concentration of CO_2 is 5%.

as the concentration of CO_2 increases and, for a given CO_2 concentration, the minimum becomes less sensitive to the balance ratio as the inerts concentration in the syngas increases. Of course, in practice, the concentration of inerts in the recycle would also be increased, which would tend to offset the latter effect. The methanol synthesis process unit must be considered in conjunction with other upstream units which produce the syngas in order to determine the optimum operating conditions. Wan and Price (1983) have considered the effects of syngas compostion in more detail than is presented here.

To maximize the conversions of CO and CO_2 to methanol and minimize the recycle rate, processing pressures should be high and temperatures low. However, at low temperatures the conversion becomes dependent upon the kinetics of the reactions; therefore the minimum temperature is dependent upon the activity of the methanol synthesis catalyst.

In the conventional high pressure process a zinc oxide - chromium oxide based catalyst is used at temperatures of 350°C or more; below 300°C this catalyst is relatively inactive. The rate expression, based on a limited number of kinetic studies, indicates a typical Langmuir-Hinshelwood mechanism in which CO, CO_2, and H_2 are adsorbed onto the surface of the catalyst (Wainwright, 1978; Kung, 1980). The effectiveness factor ranges from 0.5 to 0.95 for industrial catalysts (Earl, 1978) and the conversion per pass is approximately 30%, based on CO (Baker et al., 1983a).

The high temperatures and pressures required in methanol synthesis also favour a number of typical Fischer Tropsch exothermic side reactions which produce higher alcohols, paraffins, and ethers (McIntosh, 1978; Smith and Wang, 1984). Due to the selectivity of the catalysts and reaction conditions employed approximately 2% of the carbon oxides in the synthesis gas are consumed in these reactions. However, high H_2 concentrations suppress the formation of higher alcohols and other contaminants such as aldehydes, ketones, ethers, and esters.

Compression of the synthesis gas is costly in terms of both capital investment and energy (McIntosh, 1978). To produce a tonne of methanol from a stoichiometric mixture of H_2 and CO requires approximately 100 to 150 kWh of mechanical energy for each doubling of the pressure. If the mechanical energy (or electricity) is derived from condensing steam turbines then the primary heat equivalent of the fuel consumed triples. The compression of syngas from 2 to 32 MPa requires 1200 to 1800 kWh of energy, which is a significant fraction of the thermal energy of 1 t of methanol (6000 kWh). The effects of gasifier operating pressure on compression requirements are considered in further detail below.

The development of more active copper-zinc catalysts allowed a reduction in the compression requirements due to lower operating temperatures (200-300°C) and pressures (5-10 MPa). Syngas compression requirements were reduced by 200 to 400 kWh per tonne of methanol and recycle requirements by 100 to 200 kWh per tonne. In addition, improved selectivity, increased yield, simplified process design, and extended catalyst life (4 years at 5 MPa and 2 years at 10 MPa) were obtained. Since its introduction in the 1960s, the "low pressure" process has largely replaced the high pressure one.

Although the higher activity of the copper-based catalysts was recognized in the 1930s, these catalysts were more susceptible to sulphur poisoning and could not be used commercially until means were available to reduce the sulphur concentration in the synthesis gas to less than 0.1 ppm of H_2S (Frank, 1982; White, 1983). By comparison, zinc oxide - chromium oxide catalysts could tolerate 30 ppm H_2S in the syngas. The contamination levels of various constituents of the syngas are given in Table 2.3. Iron and nickel carbonyls, formed by the reaction of the syngas with some steels, can poison the catalyst with Fe and Ni, thus enhancing undesirable side reactions (Hamilton, 1978). Alkanes in the range C_2 to C_{20} can be produced in the ppm range by the Fischer Tropsch reaction; however, concentrations can vary from 10- to 100-fold depending on the iron in the system and its activity (Kirk and Othmer, 1978). Nickel contamination of copper-based catalysts has also been reported (Frank, 1982). In order to compensate for the side reactions, as well as the purge gas loss, a balance ratio of approximately 2.1 to 2.2 (Stratton et al., 1982) is used.

A purge gas stream is used to control the concentration of nonreactive components in the recycle gas and contains a substantial quantity of H_2, CO, and CO_2 besides inert gases such as CH_4, N_2, etc. When the concentration of CH_4 exceeds approximately 4% then steam reforming of the purge

Table 2.3 Potential methanol synthesis catalyst poisons[1]

Constituant	Information
Sulphur (H_2S, COS, CS_2)	Poison: wide range of minimum concentrations specified in literature Range: Cu-Zn-Cr: 0.03 to 0.2 ppm ZnO: 3 to over 30 ppm
Chloride	Poison: minimum concentration for Cu-Zn-Cr catalysts: 0.2 ppm
NH_3	Poison (reversible) at concentrations exceeding 150 ppm
Fe, Ni	Possible poison: form carbonyls with CO which catalyze CH_4 formation
CH_4	Inert
C_2H_4 and higher olefins	Possible poisons
C_2H_2	Poison for ZnO catalyst at concentrations exceeding 3 ppm, but various claims in literature
Oil mist	Possible poison at modest amount
Particulates	Possible poison

[1] Sources: SERI (1979), Wan et al. (1979), Hamilton (1978), Frank (1982), Goudeau et al. (1983).

stream and recycling is warranted. The optimum pressure of the methanol synthesis unit can then increase from 5 to 7 MPa (Wan, 1982).

Data from kinetic studies on the low pressure synthesis have been analyzed using reaction equations proposed for the high pressure synthesis. However, model discrimination has not been performed and it is unlikely that the reaction mechanism for the copper-based catalyst is identical to that of the zinc oxide - chromium oxide catalyst (Wainwright, 1978).

At the operating conditions employed in the low pressure process the conversions are limited by thermodynamic considerations and values quoted in the literature range from 10% to 50% per pass (Baker et al., 1983a; Hamilton, 1978; Frank, 1982). The recycle ratio is normally between 2.5

and 5 and overall CO and CO_2 conversions can approach 99% and 78%, respectively (Hamilton, 1978).

The two most common low pressure methanol synthesis processes are those of ICI and LURGI whose major difference involves the method of catalyst temperature control, hence heat removal. Temperature is controlled by the generation of steam within the LURGI reactor, shown in Figure 2.3, and by the "cold shot" technique (inter-bed gas quenching) in the ICI reactor, shown in Figure 2.4 (Beenackers and Van Swaaij, 1983). The efficient recovery of the heats of reaction of equations [1] and [2] are crucial to the process economics. The LURGI system is somewhat more efficient than the ICI in that the heat of reaction is used for the production of 4 MPa steam rather than for boiler feed water (BFW) heating (Lindman et al., 1981).

An alternative synthesis process under development is CHEM SYSTEMS, a three-phase process which is similar in concept to the liquid phase Fischer Tropsch synthesis (Kölbel and Ralek, 1980). In the CHEM SYSTEMS process a copper-based catalyst is either fluidized or entrained in an inert hydrocarbon liquid as shown in Figure 2.5 (Beenackers and Van Swaaij, 1983). It is claimed that this liquid allows more efficient control of the reactor temperature than in the gas phase processes, resulting in higher methanol yields and maximum recovery of the heat of reaction as usable steam (Frank, 1982, 1984; Sherwin and Blum, 1976). Several types of hydrocarbon liquids have been tested but the preferred type is an aliphatic liquid with a

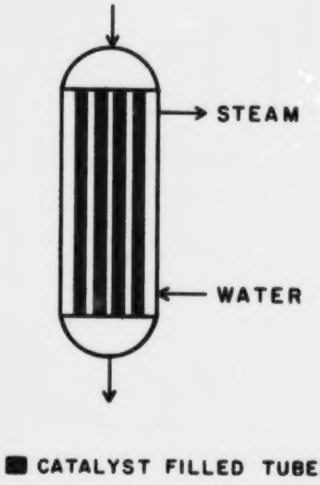


Figure 2.3. LURGI methanol reactor.

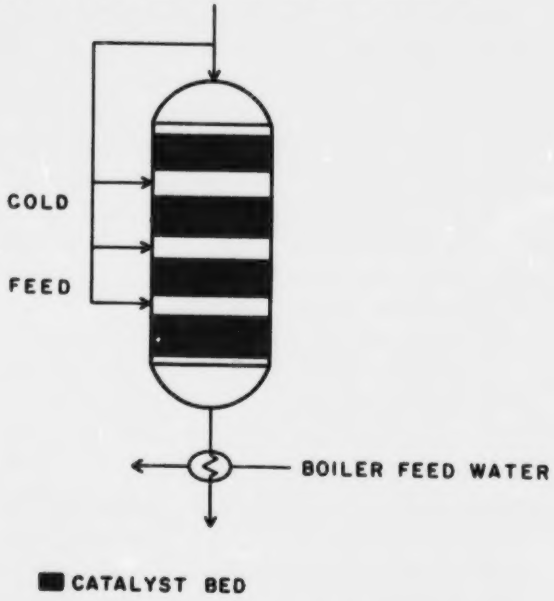


Figure 2.4. ICI methanol reactor.

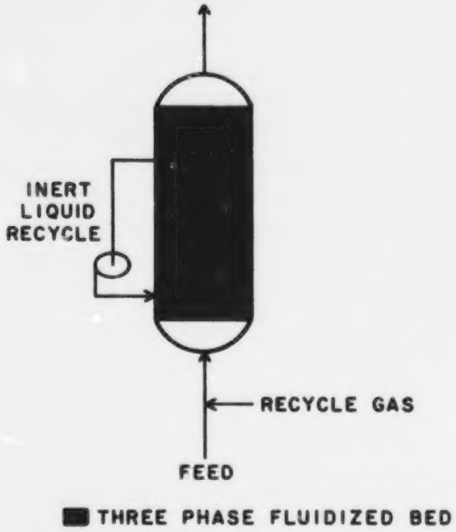


Figure 2.5. Chem Systems methanol reactor.

carbon number range from C_{14} to C_{21}. It is 72% paraffinic and 28% naphthenic and has a boiling range of 270 to 350°C. An oxygenated hydrocarbon, ethylene glycol, was tested but decomposed under reaction conditions.

In the liquid phase process a CO-rich syngas, as would be produced by the gasification of biomass ($H_2/CO = 0.6$, $CO_2 = 5\text{-}15\%$, inerts = 1%), can be processed without significant loss in catalyst activity (Frank, 1984). In this case the reduction in the catalyst activity was similar to that in a conventional gas phase synthesis in which the syngas has a much lower CO concentration and a balance ratio in excess of 2.0. However, the selectivity of the catalyst is reduced when a CO-rich gas is processed and higher alcohols are produced (Frank, 1982). At 250°C and 5.3 MPa, a 24% CO conversion can be obtained in a balanced gas, while an 8 to 9% conversion can be achieved in a CO-rich gas (Frank, 1984). In comparison a low pressure gas phase process would yield a 4 to 5% conversion for the latter gas composition (Reed, 1976).

Carbon dioxide appears to act as a catalyst promotor under operating conditions in which CO_2 conversion is expected to be low due to thermodynamic constraints (Frank, 1982). For a balanced gas the optimum CO_2 concentration for maximum methanol productivity is 4 to 5% (Frank, 1984). The minimum CO_2 concentration recommended by vendors of the gas phase processes ranges from 2 to 6% (Stratton et al., 1982). It is claimed that the conversion of CO_2 to methanol approaches 60 to 90% of the predicted equilibrium values for the liquid phase process when the syngas contains high concentrations of CO_2 (7-14%) and H_2 (75%) (Frank, 1984).

A comparison of the process efficiencies of the liquid phase and vapour phase processes are given in Table 2.4 (Simons Resource Consultants and B.H. Levelton & Associates Ltd., 1984). The liquid phase process offers the potential of a 3% increase in efficiency over the vapour phase; however, further process development is required.

The crude methanol produced by the gas or liquid phase processes can be purified by distillation. The complexity of the distillation depends upon the quality of the crude methanol and the desired purity of the product methanol. In the production of fuel grade methanol for blending with gasoline, the production of higher alcohols that would act as co-solvents would be beneficial; therefore distillation requirements would be reduced. Catalysts having lower selectivity with respect to methanol are currently under development; however, this topic is beyond the scope of the present paper.

Table 2.4. Comparison of methanol synthesis processes[1]

	ICI[2]		Lurgi[2]		Chem Systems[2]	
Pressure, MPa	5.17	10.3	3.445	10.3	3.445	7.58
Energy balance, GJ/t of CH_3OH						
Syngas	27.36	27.36	27.36	27.36	27.36	27.36
Power feed compression	0.93	2.88		2.88		2.0
Gas recycle	1.07	0.29	1.62	0.31	0.64	0.16
Oil circulation					0.31	0.14
TOTAL INPUT, GJ/t	29.35	30.53	28.97	30.56	28.31	29.64
Methanol	22.43	22.43	22.43	22.43	22.43	22.43
Recovery heat	1.34	1.36	2.73	2.79	2.99	3
Purge gas	1.15	1.16	1.15	1.17	1.15	1.38
TOTAL OUTPUT, GJ/t	24.92	24.95	26.31	26.39	26.57	26.81
PROCESS THERMAL EFFICIENCY, %	84.9	81.7	90.8	86.4	93.8	90.5

[1] Reference: Simons Resource Consultants and B.H. Levelton & Associates Ltd. (1984).

[2] ICI, Multi-bed, adiabatic quench system; Lurgi, Tube-wall, isothermal reactor system; Chem Systems, Liquid phase reactor system.

3. GASIFICATION

3.1 Thermodynamics of Gas-Char Reactions

Although the approach to equilibrium is dependent upon the temperatures, residence times, and gas-solid contacting methods used in gasifiers, thermodynamic analysis is of value in predicting trends in syngas composition. Reactions, given in Table 3.1, which are important in the modelling of gasification include the Boudouard, carbon-steam, and carbon-hydrogen. Results from SERI (1979) are given below for the gasification of wood, having an ultimate analysis of 52.5% C, 6.16% H, 41.24% O, and 0.1% N. Oxygen, rather than air, is the only case considered since nitrogen could represent approximately 40% of the syngas composition if air were used and would result in prohibitively high compression and recycle costs as well as undesirable side reactions and catalyst deactivation.

The adiabatic flame temperature for the gasification of dry wood with oxygen is given in Figure 3.1 as a function of the equivalence ratio, which is defined as the oxidant-to-fuel weight ratio divided by the stoichiometric weight ratio,

$$\Phi = \frac{O_2 \text{ (used)}}{\text{Fuel}} \times \frac{\text{Fuel}}{O_2 \text{ (stoichiometric)}}$$

When $\Phi = 0$ no oxidant is present and the wood is pyrolyzing (discussed below). When $0.225 > \Phi > 0$, the wood is being gasified. When $\Phi = 0.225$ the slope of the flame temperature - equivalence ratio curve changes dramatically and corresponds to the point at which solid carbon becomes unstable (disappears). It is also the point at which the chemical energy in

Table 3.1. Thermochemistry of carbon gasification at 500°C[1]

Reaction		Thermochemistry ΔH_{500}, kJ/mol
$C + CO_2 = 2CO$	(Boudouard)	172
$H_2O + CO = CO_2 + H_2$	(Water gas shift)	2.9
$H_2O + C = CO + H_2$	(Carbon steam)	175
$C + 2H_2 = CH_4$	(Carbon hydrogen)	-75
$C + O_2 = CO_2$	(Combustion)	-394

[1] Reference: Overend (1982).

the gas is maximized and is the preferred operating point for a gasifier. At higher ratios combustion reactions dominate and the gas temperature increases rapidly. Under actual gasification conditions heat losses will occur and the actual flame temperature will be less than the adiabatic one. Also, at temperatures less than 550°C the rate of the gas phase reactions will be so slow that equilibrium conditions will not prevail and substantial deviations from the curve will occur in practice.

The estimated composition of syngas produced by gasification at atmospheric pressure with oxygen is shown in Figure 3.2. At $\Phi = 0.225$ the balance ratio is approximately 0.57 and is too low for the synthesis of methanol using gas phase processes. The balance ratio can be increased by using the water gas shift reaction and will be discussed in further detail below.

Pressure, in the range of 101.3 kPa to 2.1 MPa, has very little effect on the adiabatic flame temperature and the syngas composition. However, the higher the pressure, the higher the reaction rates and, thus, the smaller the gasifier and the lower the compression requirements. For pressurized gasification of 1 g of dry wood 0.33 g of O_2 must be compressed compared with 1.33 g of raw syngas for unpressurized gasification. The effect of gasification pressure on power consumption has been investigated by Guzdar and Harvey (1982). The results of their findings are presented in Figure 3.3 and show that the total compression energy requirement is 25% less in going from 100 kPa to 2.1 MPa operating pressure.

The carbon-steam reaction and the water gas shift reaction increasingly affect the syngas composition when wet biomass is gasified or steam

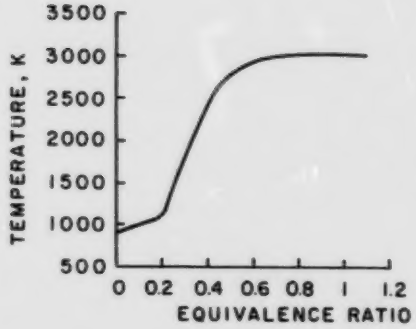


Figure 3.1. The effect of equivalence ratio on the adiabatic flame temperature for the oxygen gasification of dry wood at atmospheric pressure (based on SERI (1979)).

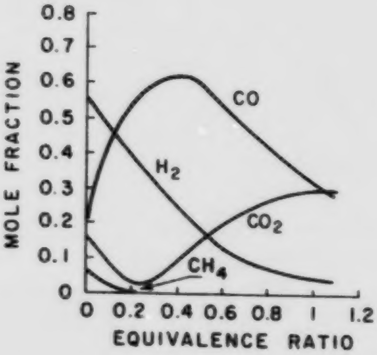


Figure 3.2. The effect of the equivalence ratio on the gas composition (dry) for the oxygen gasification of dry wood at 101 kPa (based on SERI (1979)).

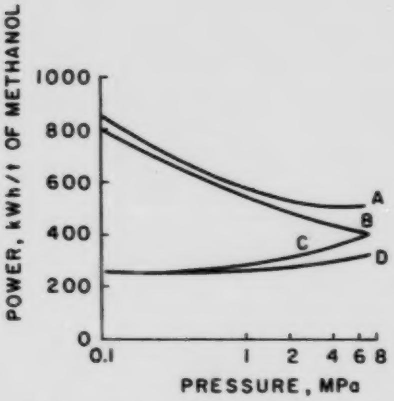
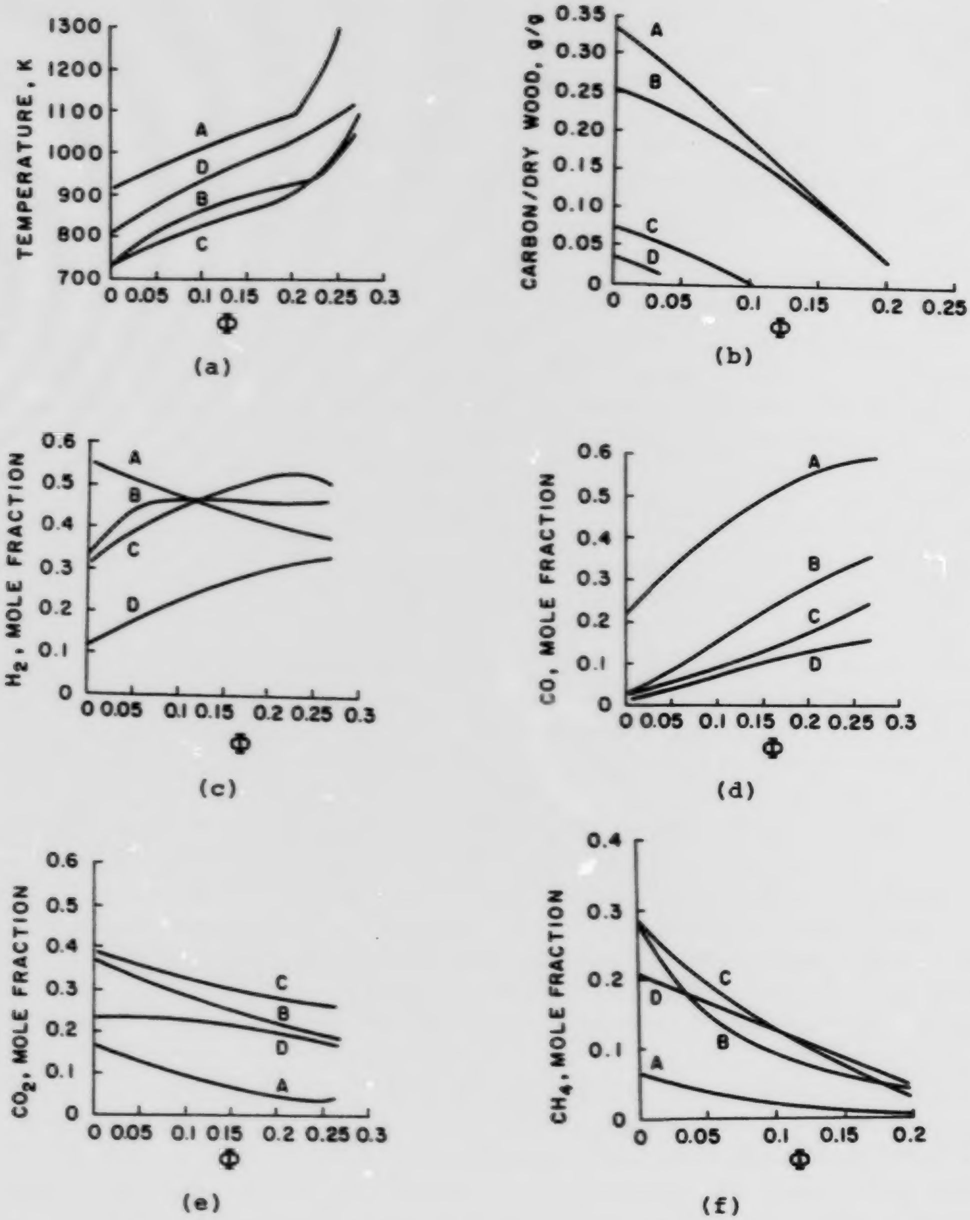


Figure 3.3. The effect of gasification pressure on power consumption: (A) solids feeding, (B) syngas compression, (C) oxygen compression, (D) oxygen generation (based on Guzdar and Harvey (1982)).

is fed to the gasifier. The gasification of wet wood (40% MC, dry basis) causes a reduction in the adiabatic flame temperature for a given equivalence ratio, as shown in Figure 3.4a. The carbon yield (Figure 3.4b), is reduced at low equivalence ratios due to the carbon-steam reaction, and results in higher syngas yields. The composition of the syngas is shown in Figures 3.4c to 3.4f. The gasification of wet biomass results in increased concentrations of CH_4 and CO_2 and a decrease in CO concentration. The effect on the H_2 concentration is dependent upon the equivalence ratio. At low equivalence ratios the H_2 concentration is reduced while at $\Phi > 0.12$ it is increased. The contributions of the carbon-steam, carbon-hydrogen, and water gas shift reactions have increased relative to that from the Boudouard. The balance ratio at $\Phi = 0.22$, corresponding to the carbon stability limit, is lower than that of dry biomass due to the high concentration of CO_2 which has been increased by the water gas shift reaction. However, removal of the CO_2 from the syngas results in a balance ratio that is greater than that for dry biomass gasified at its carbon stability limit, $\Phi = 0.225$, and again with CO_2 removal. Although the syngas yield reduced, the requirement for shifting external to the gasifier is reduced.

The effects of steam (730°C) addition are also shown in Figures 3.4a to 3.4f. The adiabatic flame temperature is reduced only slightly at $\Phi \leq 0.23$, but the carbon yield is significantly reduced. The changes in



(a) (b)

(c) (d)

(e) (f)

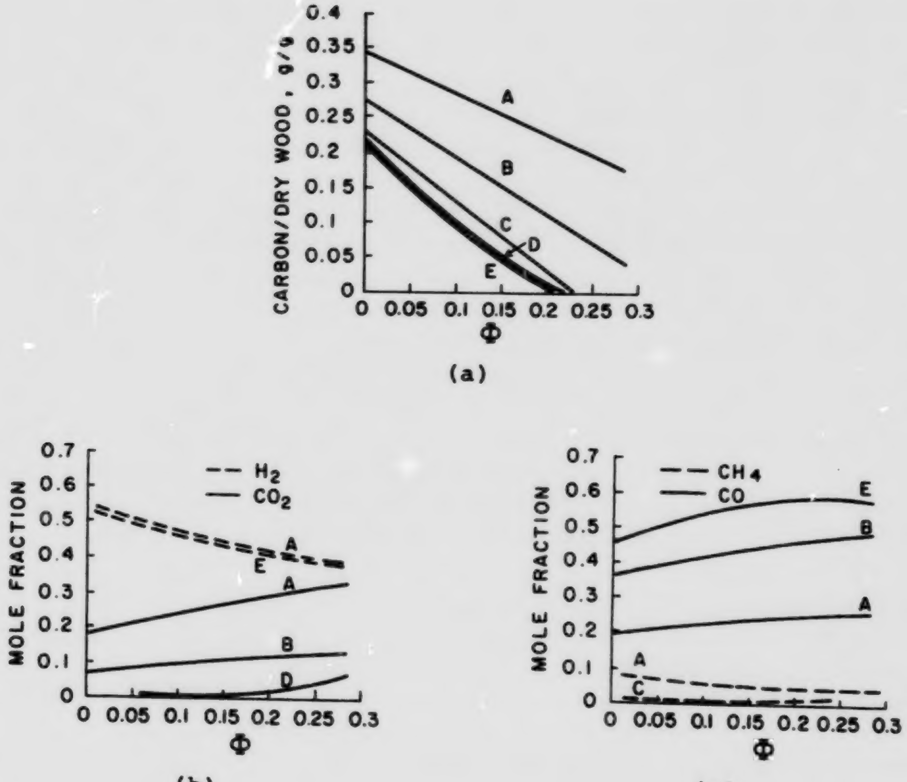
Figure 3.4. The effect of water on the (a) adiabatic flame temperature, (b) carbon yield, (c) H_2 concentration, (d) CO concentration, (e) CO_2 concentration, (f) CH_4 concentration. (A, dry wood, no steam addition, atm. pressure; B, MC = 40% (dry basis), no steam addition; C, MC = 40% (dry basis), steam/dry wood = 0.6/1, atm. pressure; D, MC = 40% (dry basis), steam/dry wood = 0.6/1, pressure = 1.5 MPa.) (SERI, 1979.)

the syngas composition are similar to those mentioned above. The balance ratio at $\Phi = 0.11$, which is the carbon stability limit in this case, is even lower than that for oxygen gasification of wet wood due to the higher concentration of CO_2. Removal of the CO_2 in this case would result in a balance ratio far in excess of two. In this case the shifting has been excessive and in practice this quantity of steam would not be fed to the gasifier.

The pressure of the gasifier has an effect on the adiabatic flame temperature, carbon yield, and syngas composition when either wet biomass or steam is used in gasification, whereas it has a negligible effect for the gasification of dry biomass. Increasing the pressure from 101.3 kPa to 1.48 MPa results in an increase in the adiabatic flame temperature and a reduction in the carbon stability limit as shown in Figures 3.4 a and b, respectively. The H_2 concentration in the synthesis gas decreases while the effect on the CO, CO_2, and CH_4 concentrations is dependent upon the steam-to-wood ratio. For the case considered, the CO and CO_2 concentrations decrease. The CH_4 concentration increases at $\Phi > 0.125$ and decreases for $\Phi < 0.125$. Concentrations are shown in Figures 3.4 c to f.

An adiabatic reaction system was considered in the preceding analysis. Therefore the temperature and hence the syngas composition were determined by the biomass composition and equivalence ratio. However, heat can be transferred from an external source, therefore the temperature may also be an independent variable. The effects of the temperature and the equivalence ratio on the carbon yield and the syngas composition are shown in Figures 3.5 and 3.6 for pressures of 101.3 kPa and 1.48 MPa, respectively. In general, as the temperature increases the yields of carbon, CO_2, and CH_4 decrease while that of CO increases. Increasing the pressure does not alter these trends, but their sensitivity increases. The H_2 concentration becomes increasingly sensitive to the temperature as the pressure increases but opposing trends are evident at 101.325 kPa compared with 1.48 MPa.

Equilibrium studies can be used to predict the operation of gasifiers only if reaction rates and residence times are sufficient for equilibrium conditions to be established. Reaction rates are dependent upon a number of parameters such as temperature, particle size and structure, thermal history, interparticle heat and mass transfer, and gas composition. Mass transfer, to and within a char particle, can have a significant impact upon the reaction rate depending upon the temperature, particle size, and mass and heat transfer coefficients and diffusivities. At temperatures under 600°C the rate of reaction is dependent upon the kinetics while at intermediate temperatures, considered to be in the range of 800 to 900°C (but dependent upon the particle size), interparticle mass transfer (pore diffusion) becomes limiting. At high temperatures, generally over 1100°C,



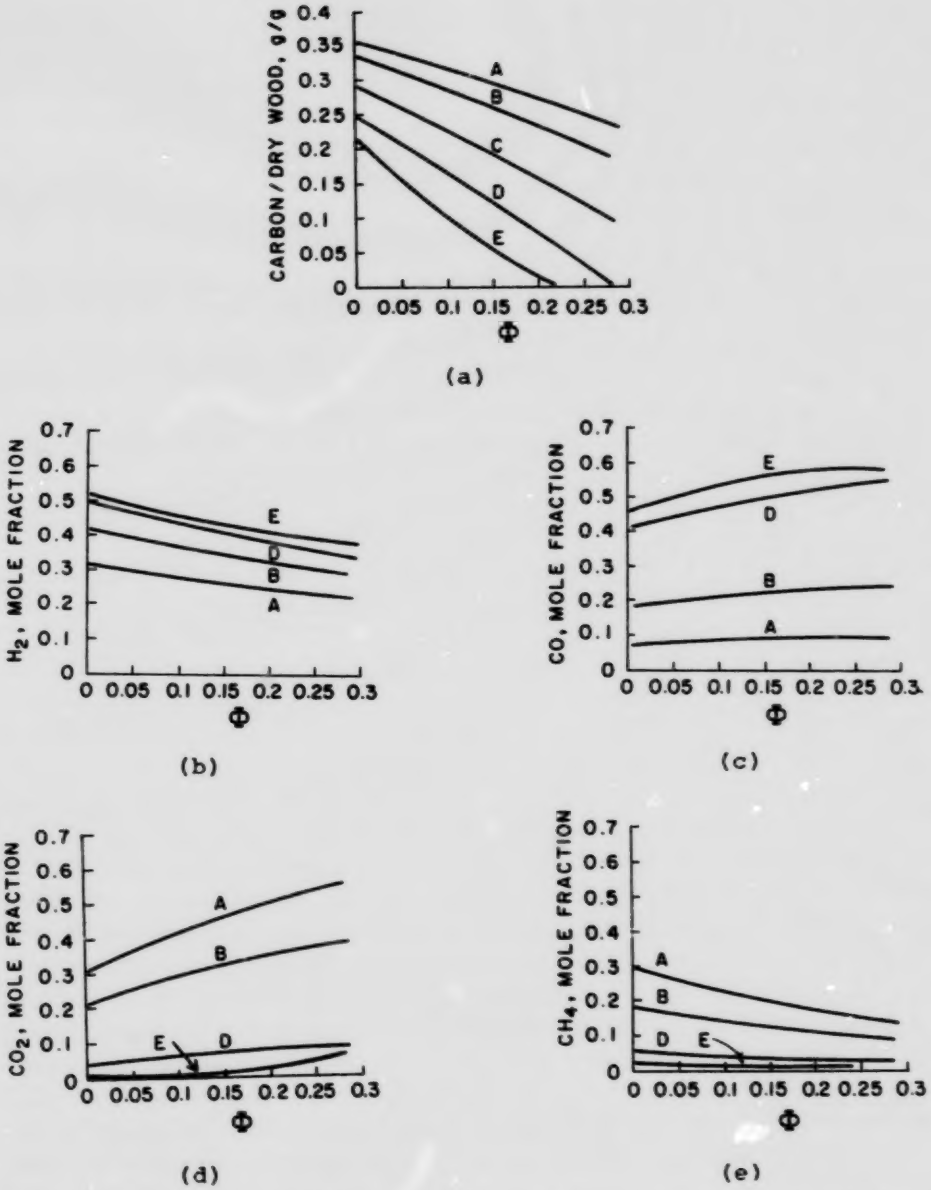
(a)

(b) (c)

Figure 3.5. The effect of temperature on (a) the carbon yield for oxygen gasification of dry wood at atmospheric pressure; (b) the H_2 and CO_2 concentrations for oxygen gasification of dry wood at atmospheric pressure; (c) the CO and CH_4 concentrations for the oxygen gasification of dry wood at atmospheric pressure. (A, 900 K; B, 1000 K; D, 1200 K; E, 1400 K.) (SERI, 1979.)

external mass transfer limits the rates of reaction. Intraparticle mass transfer is affected by particle porosity, which is dependent upon the thermal history of the char, and on the number of active carbon sites, which are associated with dislocations, edges, and mineral matter. Sintering can have an adverse effect by reducing both the porosity of the particle and the number of active sites.

Gasification reactions are affected by particle characteristics and mass transfer to varying degrees. The Boudouard, water gas shift, and the carbon-steam reactions are heterogenous and are affected by adsorption and desorption characteristics of the reactants and products. However, the water gas shift reaction can also occur homogenously at temperatures over 1100°C. The steam-carbon reaction is several times faster than the Boudouard reaction and is not affected by pore diffusion to the same extent,



(a)

(b)

(c)

(d)

(e)

Figure 3.6. The effect of temperature on the (a) carbon yield for the oxygen gasification of dry wood at pressures of 1.5 MPa, (b) H_2 concentration for the oxygen gasification of dry wood at 1.5 MPa, (c) CO concentration for the oxygen gasification of dry wood at a pressure of 1.5 MPa, (d) CO_2 concentration for the oxygen gasification of dry wood at a pressure of 1.5 MPa, (e) CH_4 concentration for the oxygen gasification of dry wood at a pressure of 1.5 MPa. (A, 900 K; B, 1000 K; D, 1200 K; E, 1400 K.) (SERI, 1979.)

since the diffusivity of steam within the pores exceeds that of CO_2. The combustion of carbon is an order of magnitude faster than the Boudouard reaction at 900°C and therefore becomes mass transfer limited at lower temperatures. The gasification of carbon is considered in further detail by Walker (1985).

Equilibrium calculations are of limited value at low temperatures since kinetic effects dominate. For pyrolysis, which occurs when $\Phi = 0$ and when temperatures are usually between 200 and 600°C, the syngas composition is dependent upon the properties of the biomass, the rate of heating, and the final temperature attained. A variety of gaseous hydrocarbons, tars, and char are obtained, as well as the gas constituents considered above.

Pyrolysis of cellulose, hemicellulose, and lignin has been conducted in the laboratory at heating rates of 0.01 to 2°C/s, which is considered to be slow, but typical of rates occurring in macroscopic pieces of carbonaceous solids. The reactivities of hemicellulose, cellulose, and lignin decrease in the order listed and most of the lignin will still be present after the first two components have decomposed. Additives have a significant impact on cellulose pyrolysis, but have only a small effect on lignin. Particle size can also affect pyrolysis since secondary reactions, auto catalysis, and physical structure come into play. These factors can affect the heat of reaction; thus pyrolysis of small particles is an endothermic process while pyrolysis of large particles may be slightly exothermic.

A problem with the slow pyrolysis studies is their limited applicability to actual gasifier operation; however, only a few studies have been conducted using rapid heat up, high temperatures, or short residence times (fast pyrolysis). In general the liquid and gas yields increase as the heating rates and temperatures increase. The syngas composition is affected by the temperature, method of gas withdrawal and quenching, and quantity of water and oxygen present. Although CO is the predominant gaseous component, the yields of H_2, CH_4, and other hydrocarbons are greater than in slow pyrolysis. At very high heating rates (flash pyrolysis) the production of olefins can be significant.

Undesirable components produced by pyrolysis, from the standpoint of methanol synthesis, are the tars, char, and gaseous hydrocarbons which would adversely affect the yield and operating conditions of the methanol synthesis process unit. The tars and char must be removed from the syngas and the hydrocarbons hydrogenated and/or reformed.

3.2 Gasifiers

The characteristics of a number of gasifiers that are currently under development are discussed below. Many of the gasifiers are currently at the bench or process development (PDU) scale and present activities are concerned with the acquisition of data which may be used in scale-up.

Gasifiers can be characterized by the reactor type: moving bed, fluidized bed, entrained bed, and molten salt; and method of heat supply: direct or indirect. With regard to the latter, the energy required to drive the Boudouard and carbon-steam reactions can be generated internally (autothermally) by the combustion of a portion of the biomass within the gasifier, or indirectly (allothermally) by heat transfer to the gasifier.

In allothermal gasification the gasifier is operated at a low equivalence ratio and heat is supplied from a separate combustor by using either a heat transfer medium or simply by heat transfer through a common wall. The source of the heat may or may not be derived from combustion of a portion of the biomass. With this method of gasification N_2 can be eliminated from the syngas and the investment in an oxygen plant can be avoided. Also, the contribution to the CO_2 concentration in the syngas due to combustion is eliminated. A cyclic operation involving combustion and pyrolysis would be required with autothermal air gasification to obtain the same effects. The cyclic method was first used in the last century for the production of medium calorific gas and the technology extensively developed and applied prior to World War II (Cleland, 1981).

A tabulation of the better-known reactor types, along with temperature distributions and feedstock particle size requirements, is given in Figure 3.7.

3.2.1 Moving Bed

3.2.1.1 Counter-current Gasifier

In the counter-current gasifier the processes of drying, pyrolysis, reduction, and oxidation occur sequentially and are separated both spatially and temporally, as illustrated in Figure 3.8. In the oxidation zone the equivalence ratios are high and char combustion releases heat and CO_2. Temperatures are of the order of 1000°C and the rate is mass transfer limited. Ash sintering can occur at these temperatures and cause problems on the grate; however, the addition of steam to the blast can reduce the temperature and reduce or eliminate this problem. The reduction in temperature is a consequence of the endothermic carbon-steam reaction (Table 3.1). The gas composition approaches the equilibrium value in this zone.

As the gas flows upwards, oxygen is consumed and the equivalence ratio drops. The reducing conditions coupled with the high temperatures make the

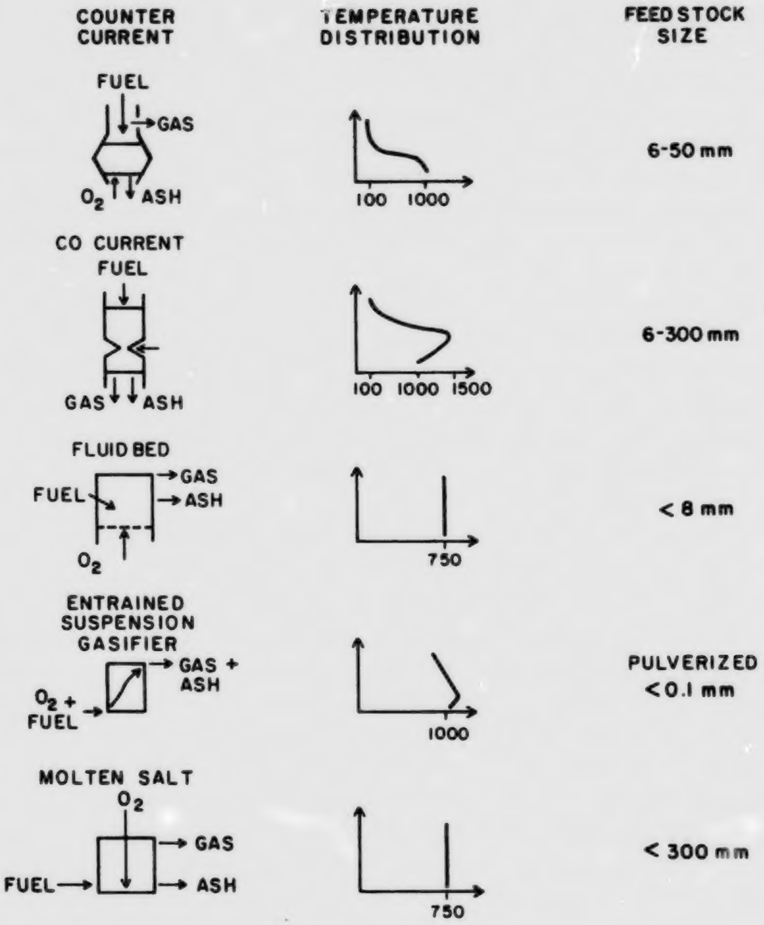


Figure 3.7. Types of gasifiers

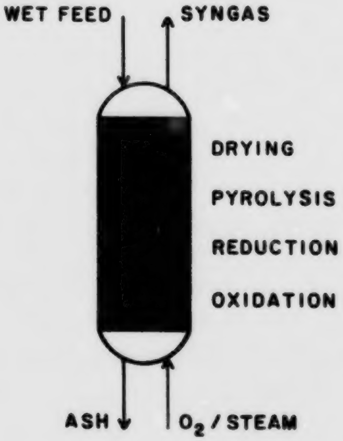


Figure 3.8. Counter-current gasifier.

Boudouard and carbon-steam reactions favourable both kinetically and thermodynamically, and the gas composition continues to approach the equilibrium value. However, the endothermicity of these reactions causes the temperature to drop to such a point that pyrolysis reactions become dominant. Since the reactions which produce equilibrium conditions in the gas phase are kinetically unfavourable at temperatures less than 600°C, the concentrations of nonequilibrium components, such as light hydrocarbons, tars, and oils, increase. Tar and oil yields ranging from 2% (Connor, 1982) to as high as 30% (Reed and Markson, 1985) have been reported. Due to the endothermicity of the pyrolysis reactions the temperature of the gas phase continues to drop until these reactions cease and only drying of the biomass occurs. The counter-current flow prevents the water removed in the drying section from influencing the gas composition through the carbon-steam reaction, but the CO/CO_2 ratio is affected since heat provided by the combustion of carbon is required for drying.

The counter-current flow in the gasifier results in good heat exchange and the sensible heat in the raw syngas is low relative to other contacting patterns. However, the high concentrations of hydrocarbons, tars, and oils make the gas unsuitable for methanol synthesis and these components must be removed either physically or by further reaction. The composition of the product gas cannot be changed significantly by adjusting the equivalence ratio since this only affects the size of the oxidation zone and hence the production rate. Although this results in a high turndown ratio (5:1) the advantage is lost since the methanol synthesis process unit must be operated at or near design for economic reasons (White, 1983). The flow of solids is sensitive to particle size distribution and shape, and channelling and carry-over can result in serious disruptions in the operation.

Many counter-current gasifiers are available commercially for the production of low calorific gas from biomass (Simons Resource Consultants and B.H. Levelton & Associates Ltd., 1984), but few are under development for syngas production. The "Davy" gasifier, marketed by D.M. International, is receiving further development and is under consideration for a Brazilian methanol synthesis process (Graham, 1982). The average compositions of the clean dry syngas, produced using oxygen and both oxygen and steam, are given in Table 3.2 (Simons Resource Consultants and B.H. Levelton & Associates Ltd., 1984). For oxygen gasification the CO_2 concentration appears to be somewhat high and the H_2 concentration low relative to equilibrium values. The H_2/CO and CO/CO_2 concentration ratios for the DMI gasifier are 0.87 and 1.89, respectively, which indicates that substantial shifting and acid gas removal would be required in order to produce a balance ratio that is suitable for methanol synthesis.

Table 3.2. Operating data for the DMI gasifier[1]

	Oxygen[2]	Oxygen and steam
Wood feed rate, kg/h	NR[3]	NR
moisture content, %	NR	NR
Steam kg/kg of dry wood	0	NR
Oxygen kg/kg of dry wood	NR	NR
Pressure, kPa	NR	NR
Temperature, °C	NR	NR
Gas,[4] Vol. %		
H_2	34.2	35.0
CO	39.4	39.9
CO_2	20.9	20.9
CH_4	4.5	3.6
C_2^+	0.5	0.2
N_2	0.3	0.4
Yield kg/kg of dry wood	1.05	NR
Higher heating value, MJ/m^3	NR	10.38
Thermal conversion efficiency (Cold), %	NR	NR

[1] References: Simons Resource Consultants and B.H. Levelton & Associates Ltd. (1984).
[2] Estimated from air blown gasification data.
[3] NR, not reported.
[4] Clean, dry gas.

3.2.1.2 Co-current

The co-current gasifier is designed to eliminate oils and tars by cracking them in the high temperature region of the reactor. Various designs can accomplish this and a schematic of a simple co-current, a "De Lacotte," and a SERI gasifier are shown in Figure 3.9 a, b, and c. The concentration of tars and oils for a simple design has been reported as approximately 500 mg/Nm^3 (Beenackers and Van Swaaij, 1984) but may range from 200 to 2000 ppm (Reed and Markson, 1985). For the SERI design the concentration is reported to be approximately 300 mg/Nm^3 (Beenackers and Van Swaaij, 1984). These concentrations represent a mass yield of the order of 0.10%, based on wood input.

In the simple co-current design heat is transferred through the bed by radiation (Reed and Markson, 1985) and can also be transferred from the raw syngas (sensible heat) through the walls of the gasifier so that it is used to dry and pyrolyze the biomass. Water vapour and pyrolysis products in

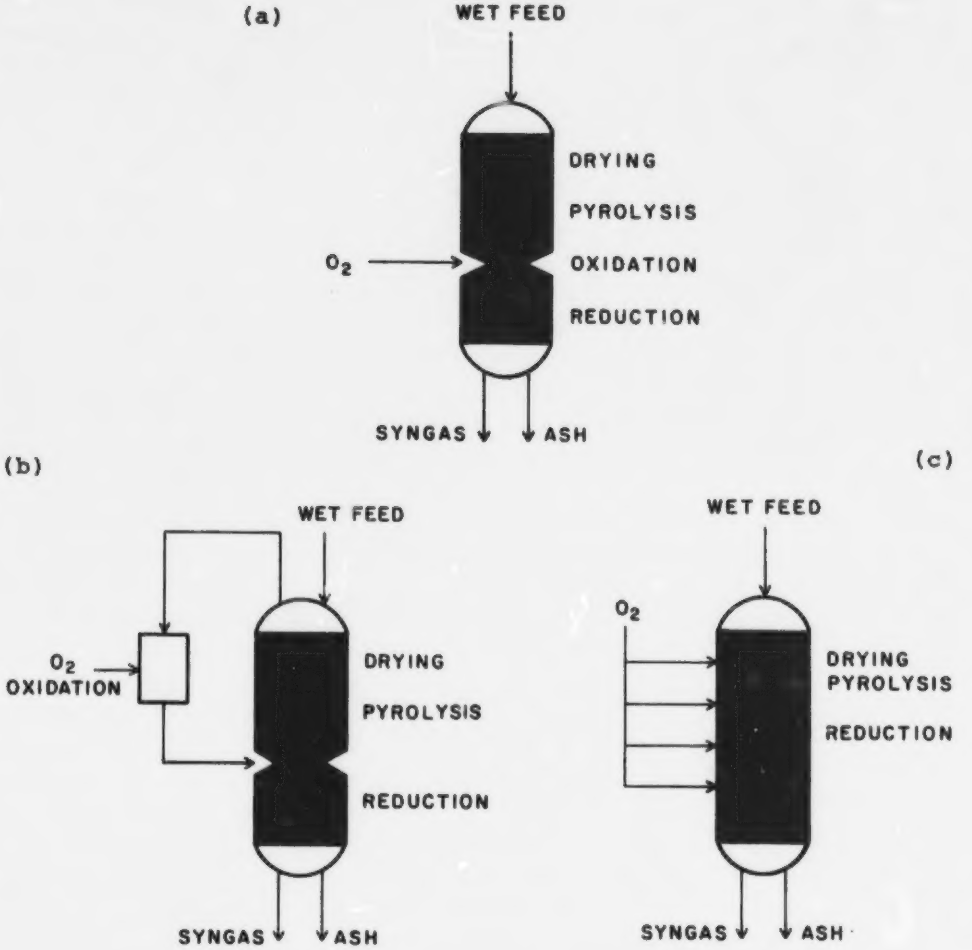


Figure 3.9. (a) co-current gasifier; (b) de Lacotte gasifier; (c) SERI

nonequilibrium proportions flow down into the high temperature oxidation and reduction zones of the reactor, where the oils and tars are cracked to light hydrocarbons and char. The reaction rates are sufficiently fast that gas compositions approach equilibrium values in this section. Most designs have a constriction or "throat" in the oxidation region which is believed to be necessary for the production of the high temperatures (Mahin, 1984). The moisture content of the biomass is a reagent in this design, which is in contrast to the counter current design; however, the solids flow problems that could develop are similar (Mahin, 1984).

In the "De Lacotte" design a counter-current flow is used in the drying and pyrolysis zones due to the good heat transfer obtained by this contacting method, and a co-current flow is used in the high temperature char bed. The gas produced in the drying and pyrolysis zones is partially combusted with oxygen in a separate reactor and then split so that a portion is recirculated through these zones and the remainder is passed through the reduction zone. The result is a gas that approaches equilibrium composition. The Creusot-Loire horizontal moving bed gasifier has design features which are similar to those of the "De Lacotte" (Simons Resource Consultants and B.H. Levelton & Associates Ltd., 1984), but also has cross flow characteristics.

The throat has been eliminated in the SERI or stratified downdraft reactor (Reed et al., 1982; Reed and Markson, 1985) and the oxygen, which is injected at a number of locations along its length, produces a temperature profile, shown in Figure 3.10, which is flatter than in the other designs. This method of oxygen injection also reduces the variation of the temperature in the radial direction and is important to the stabilization of the reaction zones. However, solids flow difficulties, such as channeling and bridging, still remain.

Dry gas compositions and operation conditions for the SERI (Wan, 1982) and the Creusot-Loire (Simons Resource Consultants and B.H. Levelton & Associates Ltd., 1984) gasifiers are given in Tables 3.3 and 3.4, respectively. The H_2/CO and CO/CO_2 concentration ratios ranges from 0.5 to 1.0 and from 1.0 to 3.5, respectively. Substantial gas processing is again required in order to produce an appropriate balance ratio with respect to the synthesis of methanol.

A problem which the above designs share, beside solids flow, is capacity limitations. Scale-up of the gasifier throat is difficult for the simple and "De Lacotte" designs, and the concentration of oils and tars increases as the capacity of the gasifier increases (Susanto et al., 1983; Beenackers and Van Swaaij, 1984). The effective distance that the oxygen can penetrate into the bed also places a size limitation on its diameter (Mahin, 1984), therefore the SERI design would also be expected to be of limited capacity.

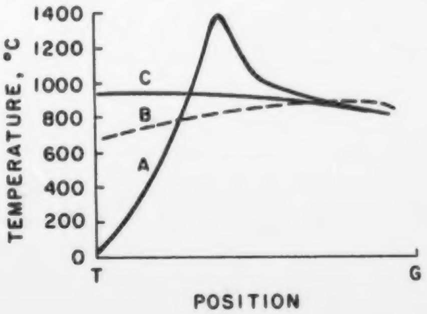


Figure 3.10. The bed temperature profile for the SERI gasifier (A, conventional down draft gasifier - O_2 injected at throat; B,C, SERI stratified gasifier - the fraction of O_2 injected at top increases going from B to C; T, top of bed; G, grate.) (Beenackers and Van Swaaij, 1984.)

Table 3.3. Operating data for the SERI gasifier[1]

Wood feed rate, kg/h	15.2	17.1	27.9	16.5	16.5	11.34
Moisture content, %	3.6	3.6	3.6	3.6	3.6	3.6
Steam kg/kg of dry wood	NA[2]	NA	NA	NA	NA	NA
Oxygen kg/kg of dry wood	0.44	0.432	0.417	0.425	0.444	NR
Pressure, kPa	101.3	101.3	101.3	101.3	101.3	101.3
Temperature, °C	900-1100	900-1100	900-1100	900-1100	900-1100	900-1100
Gas,[3] Vol. %						
H_2	31.58	31.56	32.87	25.09	26.84	30.2
CO	48.15	40.62	49.74	45.16	51.1	49.2
CO_2	14.72	18.76	14.61	18.18	14.51	17.5
CH_4	2.23	3.90	2.77	4.06	3.92	2.30
C_2^+	N[2]	N	N	0.25	N	N
N_2	3.32	5.15	2.76	7.27	3.61	0.80
Yield (carbon basis), %	NR[2]	99.29	99.00	100.00	100.00	
Higher heating value	NR	NR	NR	NR	NR	NR

---

[1] Reference: Reed et al. (1982).

[2] NA, not applicable; NR, not reported; N, negligible.

[3] Clean, dry gas.

Table 3.4. Operating data for the Creusot-Loire downdraft gasifier[1]

Wood feed rate, kg/h	~1000
Moisture content, %	15-45
Steam kg/kg of dry wood	NA[2]
Oxygen kg/kg of dry wood	0.35-0.4
Pressure, kPa	101.3
Temperature, °C	NR[2]
Gas,[3] Vol %	
H_2	29.4
CO	31
CO_2	31.4
CH_4	2.2
C_2^+	N[2]
N_2	6
Yield (carbon basis), %	99.3[4]
Higher heating value, MJ/m^3	8.11

[1] References: Simons Resource Consultants and B.H. Levelton & Associates Ltd. (1984).

[2] NA, not applicable; NR, not reported; N, negligible.

[3] Clean, dry gas.

[4] Estimated using gas composition reported and 38.7 mol of H_2 and CO per oven dried kilogram of wood at 20% moisture content.

3.2.2 Fluidized Bed

Biomass is fed into a high temperature fluidized bed in this type of gasifier; thus high heat transfer rates result in rapid drying and pyrolysis, and high reaction rates for reduction. A low yield of highly reactive char results in high syngas yields, and a wide range in particle sizes can be accommodated. Therefore, the fluidized bed gasifier has a very high throughput compared to the moving bed gasifiers, and scale-up solids flow problems are reduced. Various fluidized bed designs which are under development are shown in Figure 3.11.

In autothermal gasification drying, pyrolysis, reduction, and oxidation occur essentially simultaneously. The moisture introduced with the biomass is vaporized and reacts with the char, and the syngas composition is dependent upon such factors as temperature, residence time, and catalytic effects of the material in the bed. Examples of autothermal gasifiers under development are the High Temperature Winkler (HTW) (Wan, 1982; Simons Resource Consultants and B.H. Levelton & Associates Ltd., 1984;

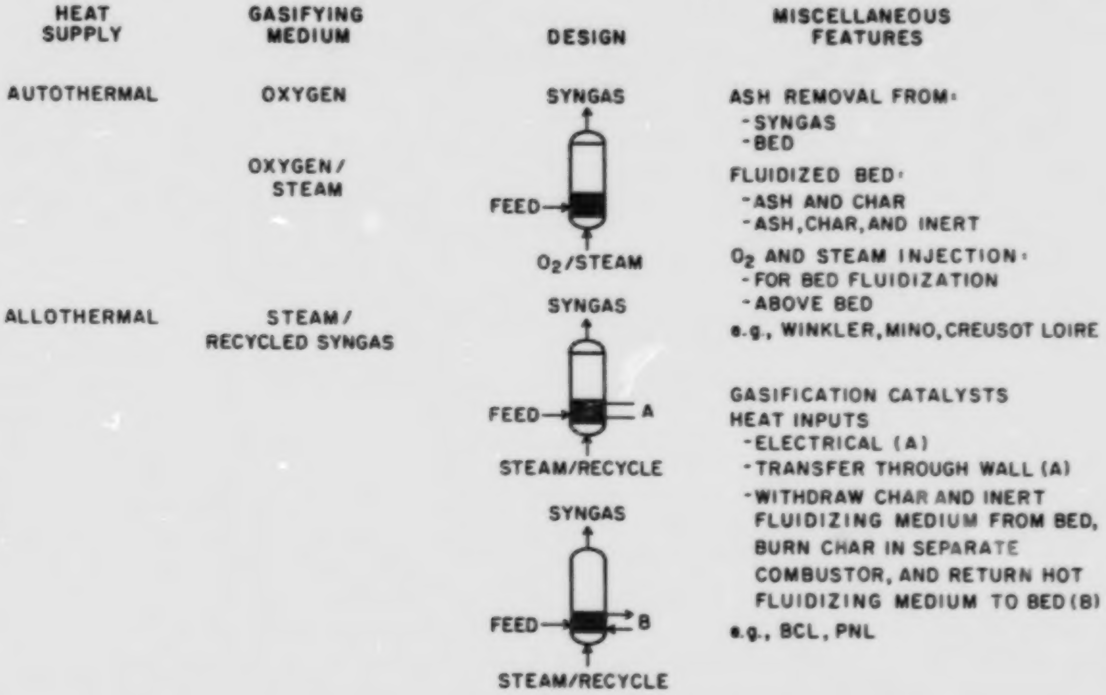


Figure 3.11. Characterization of fluid bed gasifiers.

Lindman et al., 1981; Schrader et al., 1984), the Creusot-Loire (Beenackers and Van Swaaij, 1983; Chrysostome and Lemasle, 1983; Simons Resource Consultants and B.H. Levelton & Associates Ltd., 1984; Lemasle, 1984; and the MINO (Beenackers and Van Swaaij, 1983; Blomkvist et al., 1983; Blackadder and Rensfelt, 1984).

The HTW gasifier, shown in Figure 3.12, was originally developed for the gasification of coal in the 1920s, but can also be adapted for biomass. The bed, consisting of a mixture of ash and biomass, in varying degrees of conversion, is fluidized by injecting oxygen and steam through nozzles that are arranged radially. The gasification temperature exceeds 900°C and ash sintering can occur. Ash agglomeration is an important factor since the particle size must exceed the critical size in order for it to be defluidized and removed from the bottom of the reactor; but it must not be excessive, otherwise the uniformity of the fluidized bed will be destroyed. Temperature, which is critical, is controlled by the injection of steam. Oxygen and steam are also injected above the fluidized bed so that hydrocarbon cracking can be induced and the composition of the raw syngas controlled. Temperatures of 1100°C are required in the freeboard gas in order

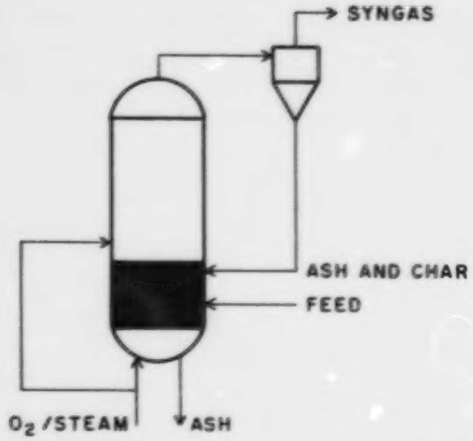


Figure 3.12. High temperature Winkler (Uhde) gasifier.

to reform methane, but soot can be produced by the cracking reactions if the temperatures exceed 900°C. Operating data for the gasification of wood are given in Table 3.5. The H_2/CO concentration ratio is approximately 1.1 and the CO/CO_2 concentration ratio ranges from approximately 1.5 to 2.3. The concentration of methane is relatively low (1%) due to the high gasification temperature in and above the fluidized bed. The carry-over of char, ash, and tar is greater in the fluidized bed than in the moving bed due to the high gas velocities required for the fluidization and must be removed prior to downstream gas processing.

The Creusot-Loire and MINO gasifiers, shown in Figure 3.13, differ from the HTW in the method of ash removal and the operating temperature. The gasifiers have been designed to operate at less than 900°C so that ash sintering is reduced and a uniform fluidized bed is produced. The ash, as well as the char carry-over, is removed from the syngas using either cyclones (Creusot-Loire) or a high temperature metal filter (MINO). In order to maintain high thermal efficiencies for the process, the char must be separated from the ash and recycled back to the gasifier or at least be used as a fuel for the generation of steam and power. The lower temperature of the gasifier is beneficial in terms of operability, but some costs are incurred with respect to syngas composition. As a consequence of the higher CH_4 concentration, the Creusot-Loire gasifier includes a thermal reformer while the MINO has a catalytic one.

The Creusot-Loire gasifier has been operated at temperatures ranging from 700 to 850°C and the reformer from 1100 to 1300°C. At these temperatures the gas is rich in hydrocarbons and the methane concentration can be up to 10%, as shown in Table 3.6. This is significantly higher than the concentration predicted by thermodynamic considerations and is high

Table 3.5. Operating data for the HTW gasifier[1]

Wood feed rate, kg/h	909	
Moisture content,[2] %	10%	
Steam kg/kg of dry wood	0.18	0.18
Oxygen kg/kg of dry wood	0.46	0.46
Pressure, kPa	1100	1100
Temperature, °C	970	970
Gas,[3] Vol. %		
H_2	32.6	33.2
CO	29.2	30.7
CO_2	19.2	13.7
CH_4	0.5	0.8
C_2^+	NR[4]	NR
N_2	NR	0.18
Yield (carbon basis), %	98.5[5]	NR
Higher heating value, MJ/m^3	NR	8.0
Thermal conversion efficiency (Cold), %	NR	80

[1] References: Lindman et al. (1981) and Simons Resource Consultants and B.H. Levelton & Associates Ltd. (1984).

[2] Dry gas.

[3] Wet basis.

[4] NR, not reported.

[5] Estimated

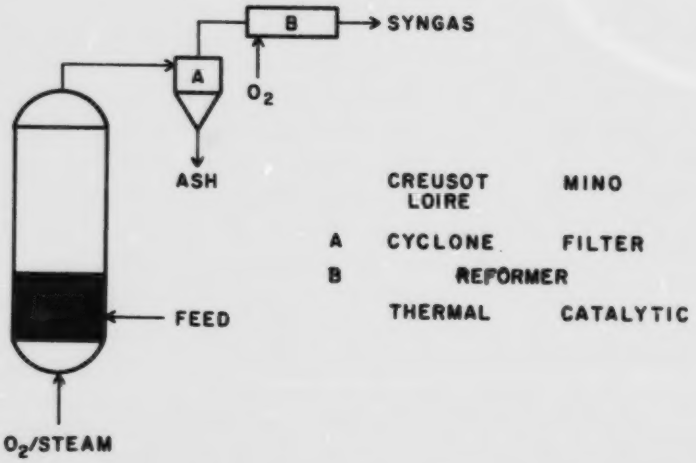


Figure 3.13. Creuset Loire and MINO gasifiers.

Table 3.6. Operating data for the Creusot-Loire fluidized bed gasifier[1]

Wood feed rate, kg/h	100-200		87.8		
Moisture content, %	20		20[2]		
Steam kg/kg of dry wood	NR[3]	NR	0.23		
Oxygen kg/kg of dry wood	NR	NR		0.46[4]	0.55[4]
Pressure, kPa	101.3	101.3	101.3		
Temperature, °C	800[5]	1200[6]	700[5]	1100[6]	1300[6]
Gas,[7] Vol. %	8	9			
H_2	19.0	NR		32.9	33.6
CO	35.0	NR		31.4	35.0
CO_2	30.0	NR		32.1	28.2
CH_4	10.0	2.4		3.2	1.5
C_2^+	3.0	0.15			
N_2	3.0	NR			
H_2O					
Yield (carbon basis), %	NR	NR		NR	NR
Higher heating value, MJ/m^3	NR	NR		8.8	8.7

[1] References: Chrysostome and Lemasle (1983) and Simons Resource Consultants and B.H. Levelton & Associates Ltd. (1984).

[2] Wet basis.

[3] NR, not reported.

[4] Total O_2.

[5] Gasifier.

[6] Reformer.

[7] Dry basis.

[8] Gasifier exit.

[9] Reformer exit.

compared to the Winkler. After reforming at a temperature of approximately 1300°C, the concentration is reduced to a level that is comparable with the HTW, but high oxygen inputs are required for the reformer and the overall equivalence ratio is greater. The high temperatures also favour soot formation due to the inverse of the carbon-steam reaction and ash may accumulate since the sintering temperature is exceeded. The H_2/CO concentration ratio is approximately 1.0 and the CO/CO_2 concentration ratio is approximately 1.2. The concentration of methane after the reformer ranges from 1.5 to 3.2%. The carbon conversion to methanol using this gasifier would be less than with the HTW.

The MINO gasification system employes a catalytic reformer so that the temperature and hence the oxygen requirements can be reduced. The lower temperature would also reduce the ash sintering problems and the soot formation. The critical element in the scheme is the development of a high temperature filter for the syngas since particulate carryover (and perhaps sulphur) could deactivate the catalyst. After reforming, the syngas has H_2/CO and CO/CO_2 concentration ratios of approximately 1.2 and 1.6, respectively. The methane concentration is less than 0.5%. Further data are given in Table 3.7.

Allothermal fluidized bed gasification is being investigated by Battelle Columbus Labs (Beenackers and Van Swaaij, 1983; Simons Resource Consultants and B.H. Levelton & Associates Ltd., 1984; Feldmann et al., 1983; Paisley et al., 1984) and Battelle Pacific Northwest Labs (Mudge et al., 1983; Baker et al. 1983a; Robertus et al., 1983; Baker et al., 1984; Simons Resource Consultants and B.H. Levelton & Associates Ltd., 1984). The Battelle Columbus Labs (BCL) process development unit, illustrated in Figure 3.14, is similar in concept to pilot plants (0.2 t/h) Andoh et al., 1979) and demonstration plants (1.5 t/h) (Kagayama et al., 1979) built in 1975 to investigate the pyrolysis of solid waste. In the BCL process steam or steam recycle gas is used to fluidize and gasify ($\Phi = 0$) the biomass at temperatures between 750 and 900°C and at rates of 2.7 $kg/(m^2s)$. The fluidized bed is composed of biomass and sand or aluminoxide, with the latter in two particle size ranges. The larger size remains within the gasifier as a stationary fluidized bed while the smaller size is elutriated with the ash and char. The solids are separated from the syngas in a cyclone and injected into a separate fluidized bed combustor where the combustion of the char produces temperatures between 900 and 1000°C. Since the rate of char combustion in conventional fluidized beds is substantially less than the gasification rate, a high throughput fluidized bed combustor was developed which could be coupled to the gasifier without causing solids flow difficulties. The hot sand is then returned to the gasifier where it provides heat for the endothermic gasification reactions. However, combustion temperatures within the range given above could cause ash sintering and operating problems could ensue (Beenackers and Maniatis, 1984).

Table 3.7. Operating data for the MINO gasifier[1]

Wood feed rate, kg/h	10		10^2		
Moisture content, %	10^3		NR^4		
Steam kg/kg of dry wood	0.46		NR		
Oxygen kg/kg of dry wood	0.17^5	0.27^6	$0.20-0.25^5$		
Pressure, kPa	3000		1000		
Temperature, °C	750^5	950^6	800^5	900^6	1100^6
Gas, Vol. %					
H_2	23.7	29.4	NR		
CO	14.5	24.2	NR		
CO_2	22.0	15.0	NR		
CH_4	12.4	0.2	NR		
C_2^+	NR	NR	NR		
N_2	0.2	0.2	NR		
H_2O	27.2	31.2	NR		
Yield (carbon basis), %	NR		NR		
Higher heating value, MJ/m^3	NR		NR		
Tar yield, wt%	NR		0.6	0.04	0.015

[1] References: Beenackers and Van Swaaij (1983), Blomkvist et al. (1983), and Lindman et al. (1981).

[2] Peat.

[3] Dry basis.

[4] NR, not reported.

[5] Gasification.

[6] Reforming.

[7] Wet basis.

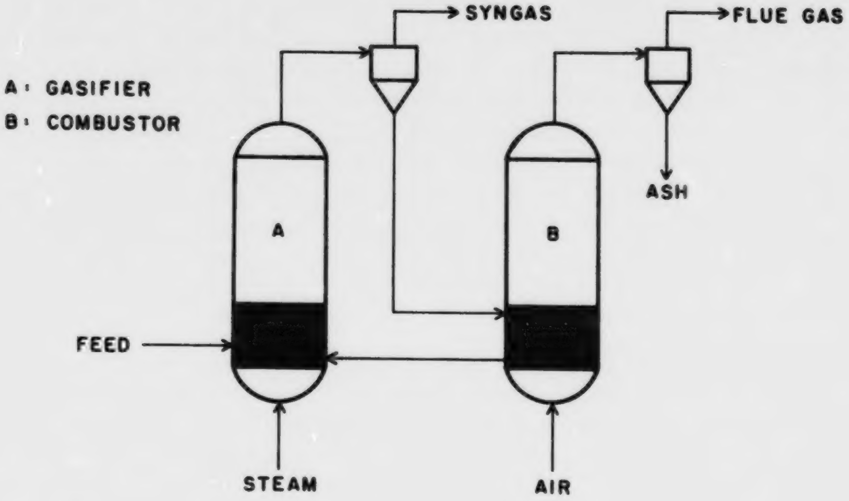


Figure 3.14. BCL gasifier

Low temperature steam gasification results in high yields of hydrocarbons, tar, and char. Hydrocarbon yields of 15 to 20%, given in Table 3.8, increase the reforming requirement, which cannot be conducted autothermally as in the case of the Creusot-Loire or MINO processes since a source of oxygen is not available. The carbon conversion to syngas is dependent upon particle size and gasifier temperature, and values from 40 to 85% have been reported (Feldman et al., 1983). Increased syngas yields can be obtained using "turbulent wake inducers," which probably affect the residence time of the entrained char particles in the gasifier. The H_2/CO concentration ratio ranges from 0.2 to 0.8, and the CO/CO_2 ratio can range from 1.8 to 7.9.

The Battelle Pacific Northwest Lab (PNL) gasifier differs from the BCL in that catalysts are used to increase cracking, reforming, shift, and gasification reactions; hence, throughput is increased, syngas composition is more compatible to the synthesis of methanol, and char yields are reduced. Gasifier temperatures of 750°C can be used due to the increase in reaction rates, which is a distinct advantage since heat transfer limitations can impose a limit on the maximum gasifier temperature (Beenackers and Van Swaaij, 1984). Although electrical heating was employed in the PDU, heat exchanger bundles inserted in the fluidized bed are envisaged in commercial units. Critical elements in this approach are catalyst activity, resistance to deactivation by carbon deposition, thermal sintering, thermal cycling, regenerability, and durability.

Table 3.9 gives results of PDU experiments for the PNL gasifier. At a gasifier temperature of 730°C and a pressure of 1 MPa uncatalyzed operation

Table 3.8. Operating data for the BCL gasifier[1]

Wood feed rate,[2] kg/h	84.5	64.5	49.1	57.3	56.4	83.2	57.3	57.3	58.6	63.2	71.8	71.8
Moisture content[2], %	5.3	5.3	8.2	8.2	8.2	6.2	6.2	6.2	4.8	9.8	12.0	12.0
Steam kg/kg of dry wood	1.2	2.6	2.5	1.6	0.4	1.9	2.6	0	2.9	2.2	2.4	2.4
Oxygen kg/kg of dry wood	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Pressure, kPa	119	129	115	115	115	126	117	129	126	118	123	124
Temperature, °C	843	809	789	821	857	799	791	830	830	827	792	810
Gas,[2,4] Vol.%												
H_2	19.9	16.3	14.7	15.4	16.6	18.7	17.2	17.1	18.1	20.6	17.7	19.6
CO	44.3	47.5	49.5	48.5	47.0	49.7	51.6	48.7	50.3	48.2	50.2	48.5
CO_2	13.7	13.4	13.9	14.0	13.4	9.62	9.4	9.0	9.6	10.0	9.7	9.9
CH_4	16.5	16.9	15.9	16.0	16.8	15.4	15.1	15.7	15.7	14.9	15.6	15.3
C_2^+	5.6	6.0	6.2	6.2	6.1	6.6	6.7	8.6	6.3	6.4	6.7	6.7
N_2												
H_2O												
Yield (carbon basis), %	86.0	79.9	73.0	73.2	79.0	64.7	64.5	66.1	69.6	76.2	68.8	72.8
Higher heating value, MJ/m^3	17.3	17.6	17.4	17.4	17.7	18.0	18.0	19.0	17.9	17.8	18.1	18.0
Thermal conversion efficiency(Cold), %	78.8	76.6	65.8	56.2	65.8	63.0	68.7	77.3	68.2	71.5	65.3	70.1

[1] References: Feldman et al. (1983)

[2] Dry basis.

[3] NA, not applicable.

[4] Inert free basis.

Table 3.9. Operating data for the PNL gasifier (dual fluidized beds)[1]

Wood feed rate,[2] kg/h	0.88	0.72	0.70	0.97
Moisture content, %	NR[3]	NR	NR	NR
Steam kg/kg of dry wood	0.9	1.1	1.1	0.86
Oxygen kg/kg of dry wood	-	-	-	-
Pressure, kPa	NR	NR	NR	NR
Temperature, °C	750	750	750	750
Gas,[4] Vol. %				
H_2	60.8	55.9	62.7	56.1
CO	23.2	20.9	19.1	24.4
CO_2	13.6	16.7	16.3	13.6
CH_4	2.6	5.6	1.7	5.1
C_2^+	0.1	0.9	0.2	0.8
N_2				
H_2O				
Yield (carbon basis), %	84	87	95	91
Catalyst	NiCuMo	NiCuMo	G-90C	G-90C
Duration of test, h	6.0	34.2	6.5	6.3

[1] References: Brown et al. (1985).

[2] Assume dry basis.

[3] NR, not reported.

[4] Dry basis.

can result in methane concentrations of 20%; however, with catalyzed operation the concentration can be reduced to between 6 and 8%. Higher syngas yields can be obtained with K_2CO_3, but char agglomeration can effect fluidization. The concentration ratio H_2/CO can range from 1.4 to 4.3, and the CO/CO_2 ratio can vary from 0.4 to 2.3.

Lurgi Kohle and John Brown/Wellman have also produced novel fluidized bed gasifiers. The Lurgi Kohle gasifier (Beenackers, 1983; Beenackers and Van Swaaij, 1983, 1984; Simons Resource Consultants and B.H. Levelton & Associates Ltd., 1984) is a fluidized bed which is operated with very high gas fluidizing velocities so that high solids entrainment occurs. The entrained solids are separated from the syngas by a cyclone and returned to the gasifier. It is claimed that this approach reduces the solids agglomeration problems, hence the fluidized bed can be operated at higher temperatures so that the concentration of hydrocarbons in the syngas can be reduced.

The John Brown/Wellman oxygen-donor fluidized bed (Beenackers and Van Swaaij, 1983, 1984) differs from the BCL gasification system in that the solid heat carrier is also a reactant which eliminates the need for both oxygen and steam as gasifying agents. The principal reactions which occur in the gasifier and oxidizer are given in Table 3.10. A demonstration plant with a capacity of 900 kg/h is currently under construction.

The Institute of Gas Technology has been involved in the development of pressurized fluidized bed gasifiers (Kosowski et al., 1984a, b; Babu et al., 1982; Evans et al., 1985). The 11 t/d unit has been operated at a wood feed rate of 8.8 t/d (1.53 kg/(m^2 s)) and at pressures up to 2.2 MPa. For operating temperatures ranging from 815 to 1000°C, the carbon conversion to syngas has ranged from 88 to 94%. The H_2/CO and CO/CO_2 ratios have varied from 1.4 to 2.4 and 0.26 to 0.64, respectively, and CH_4 and C_2^+ concentrations from 5.3 to 7.4% and 0 to 1.17%, respectively. However, these concentrations are based on a wet gas that contains high concentrations of inerts (N_2 and Ar). Inerts concentrations varied from 14.9 to 21.9%. Operating data are given in Table 3.11. As mentioned above, ash sintering may be a problem at these temperatures and fluidization could be adversely affected.

3.2.3 Entrained Bed

Entrained bed gasification, developed for coal by Texaco and Koppers-Totzek, has been tested with wood (White, 1983) and peat (Maly and Sabri, 1980; Lindman et al., 1981). Small particle sizes and high temperatures are required due to the short residence times involved. If further experimentation indicates that particle size must be less than 0.1 mm then this approach will be in jeopardy since high energy costs will be incurred for comminution (White, 1983; Lindman et al., 1981; Bridgewater, 1984). In addition, the syngas exits the gasifier at a high temperature; therefore extensive heat recovery is required, and it may be somewhat difficult to control this reactor due to the short residence time involved and the problem of feeding fibrous material uniformily. The scale of operation, 500 t/d, may also impose high operating costs (Beenackers and Van Swaaij, 1984).

Table 3.10. Principle reactions of the oxygen donor process[1]

Oxidizer	$CaS + air = CaSO_4$ $C + air = CO_2$
Gasifier	$CaSO_4 + 4H_2 = CO_2$ $CaSO_4 + 4CO = CaS + 4CO_2$ $C + H_2O = CO + H_2$ $C + CO_2 = 2CO$

[1] Reference: Beenackers and Van Swaaij (1983).

Table 3.11. Operating data for the IGT pressurized fluidized bed gasifier[1]

Wood feed rate,[2] kg/h	339	284	300	295	281	303
Moisture content, %	8.35	9.50	9.70	10.47	10.72	11.15
Steam kg/kg of dry wood	0.86	0.78	0.66	0.86	0.96	0.73
Oxygen kg/kg of dry wood	0.23	0.28	0.38	0.19	0.27	0.25
Pressure, kPa	2230	2230	2130	2130	2150	2130
Temperature, °C	816	899	982	754	816	821
Gas,[3] Vol.%						
H_2	10.58	11.82	13.58	9.62	8.08	9.97
CO	6.09	6.38	9.92	4.07	5.36	6.63
CO_2	15.63	17.15	15.49	15.92	13.98	15.04
CH_4	7.39	7.39	5.29	6.20	5.95	6.78
C_2^+	0.45	0.32	0.0	1.17	0.65	0.71
N_2 + Ar	17.08	15.42	20.76	14.93	20.54	21.87
H_2O	42.78	41.52	34.96	48.09	45.44	39.00
Yield (carbon basis), %	88.2	92.2	94.2	82.3	88.2	90.5
Higher heating value,[4] MJ/m^3	12.8	12.6	10.9	13.3	12.9	13.2
Thermal conversion efficiency (Cold), %	75.1	76.2	73.9	68.8	71.3	76.4
Liquid yield (carbon basis), %	3.8	2.2	0.6	4.9	3.8	2.2

[1] References: Evans et al. (1985).

[2] Dry basis.

[3] Wet basis.

[4] Inert free.

3.2.4 Molten Salt

An alternative to the fluidized bed, which avoids the problems of ash sintering and reduces the carry-over of flyash and particulate material, is the molten salt gasifier (Moffatt and Anand, 1984), shown in Figure 3.15. In this process biomass is gasified with oxygen and steam in a salt bath. The results of bench scale tests, using Na_2CO_3 and temperatures between 800 and 1000°C, are given in Table 3.12. Under the conditions employed char yields were under 0.5%, but methane concentrations were generally over 5%. The yields of hydrocarbons may be reduced if it becomes possible to operate at higher temperatures. The H_2/CO and CO/CO_2 ratios lie between 0.6 and 1.7, and 1.1 and 1.7, respectively; however, the effect of salt composition on product distribution has not been thoroughly investigated.

3.2.5 Summary

Although the availability of operating data has in some cases been relatively restricted and the scale of operation has been low, valid conclusions and comparisons can be made between the various types. Problems with the fixed bed gasifiers include the sensitivity of solids flow to feedstock physical characteristics, the quality of the syngas produced by the counter-current gasifier, and the scale-up of the co-current gasifier. Some of these problems can be avoided with other designs; therefore the fixed bed gasifier will probably not be used to any great extent for the production of methanol.

The fluidized bed gasifier has a higher productivity ($m^3/(m^2\ s)$) than the fixed bed gasifier, does not have the scale-up problems and has a

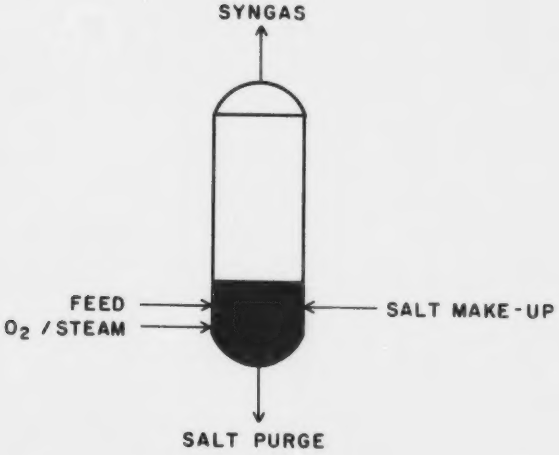


Figure 3.15. Molten salt gasifier.

Table 3.12. Operating data for the molten salt gasifier[1]

Wood feed rate, kg/h	1.16	2.14	2.53	2.52	2.60	2.56	1.22
Moisture content, %	5.35	5.35	5.35	5.35	5.35	5.35	5.35
Steam kg/kg of dry wood	1.02	0.98	0.44	0.86	0.45	0	0.96
Oxygen kg/kg of dry wood	0.51	0.47	0.36	0.37	0.38	0.31	0.28
Pressure, kPa	101.3	101.3	101.3	101.3	101.3	101.3	101.3
Temperature, °C	1002	1003	875	882	1000	874	822
Gas, Vol.%							
H_2	17.36	18.32	21.40	20.73	22.78	22.15	18.98
CO	14.03	15.50	20.80	15.77	22.99	36.44	13.05
CO_2	22.10	21.03	19.62	18.46	22.07	19.68	21.15
CH_4	4.45	5.03	5.65	4.27	6.22	7.43	3.89
C_2^+	0.26	0.42	1.61	1.28	0.59	2.40	1.12
N_2	0.10	0.10	0.12	0.10	0.15	0.20	0.11
H_2O	41.70	39.60	30.80	39.40	25.20	11.70	41.70
Yield (carbon basis), m^3/kg	2.6	2.4	2.0	2.5	1.7	1.2	2.2
Higher heating value[2], MS/m^3	9.6	10.3	11.8	11.2	11.0	12.8	10.3
Molten media	Na_2CO_3	Na_2CO_3	Na_2CO_3	Na_2CO_3	Na_2CO_3	Na_2CO_3	Na_2CO_3-$NaCl$[3]

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[1] References: Moffatt and co-workers (1982, 1984).

[2] Dry basis.

[3] Na_2CO_3 : NaCl = 3:1 (weight basis).

yield of oils and tars which is intermediate between the counter-current and the co-current designs. However, the entrainment of solids such as ash and char is greater than the fixed bed. Therefore gas clean-up and processing costs will be higher. Since ash sintering can affect fluidization, the trend is to operate the bed at low temperatures. This increases the yields of CH_4 and C_2^+, which must be reformed and possibly hydrogenated, and oils and tars, which must be physically removed from the syngas. Catalysts can help to alleviate these problems by increasing the yield of syngas and modifying its composition, but considerable development is required. Finally, allothermal gasification is possible with this type of gasifier, but the reduced capital and operating costs from elimination of the oxygen plant are offset to some extent by the increased gasifier capital cost and operational complexity. Although the fluidized bed gasifier is deficient in many respects it offers the best potential for near-term production of syngas for methanol production.

Pilot plants that are under construction in Europe and Canada will provide valuable information on fluidized gasificaton. The Commission of European Communities (Beenackers, 1983) is sponsoring projects that will test pressurized oxygen gasification in conventional fluidized beds (Creusot-Loire), oxygen gasification in a circulating fluidized bed (Lurgi), the Oxygen Donor Process (John Brown/Wellman), and wood pyrolysis followed by secondary gasification of the pyrolysis products with oxygen (AGIP Nucleare/Ital Energie (Cogliati and Missoni, 1985)). A pilot plant based on the MINO process has been constructed at Studsvik Energitetnik AB under the auspicies of the Swedish government, and a pilot plant, BIOSYN, is under construction in Canada to test oxygen gasification in a conventional fluidized bed (Gravel, 1984).

The entrained bed gasifier (Koppers Totzek) can produce a syngas which is low in hydrocarbons, oils, and tars, but extensive feedstock preparation, dynamic control problems, and small scale may prevent its use with biomass. Further testing is required.

The molten salt gasifier can avoid some of the problems that are associated with fluidized bed gasifiers, such as poor fluidization due to ash sintering effects and the high carry-over of solids. High temperature operation is also possible which will reduce tar, oil, and gaseous hydrocarbon yields. The feasibility of this approach will be based on materials considerations, such as corrosion, and the effect of ash on the molten salt. Corrosion problems are expected to be less than would be experienced with coal due to the lower operating temperature, quantity, and composition of inorganic constituents. Further experimentation with biomass is required.

4. OXYGEN PRODUCTION

Oxygen is required for gasification and for reforming, if conducted autothermally, as discussed above. It can be produced by a number of means such as cryogenic, pressure electrolysis, and pressure swing absorption (PSA), and has been considered by Reed (1982) and Moffatt and Anand (1984).

The cryogenic process is the preferred production method when 90 to 2000 t/d are required, which is the case for the plant scales under consideration - approximately 350 to 450 t/d of oxygen are required for the production of 500 t/d of methanol. In this process air is compressed to approximately 600 kPa and then expanded to produce liquid air at -192°C. Water and CO_2 are removed and the O_2, N_2, and Ar are then separated by distillation. Oxygen is produced at approximately 200 kPa and compressed to whatever pressure is required for its use. Power requirements of approximately 440 kWh/t of O_2 produced have been reported, but it is very dependent upon plant efficiencies, oxygen pressure, and purity, etc. Power costs can be responsible for 40 to 80% of the final oxygen cost. Capital costs are sensitive to plant capacities and range from $27 000 (t/d) for a 2000 t/d plant to $45 000 (t/d) for a 90 t/d plant (based on Reed (1982)).

Pressurized electrolysis of water is an alternative to the cryogenic process and can produce oxygen and hydrogen at pressures up to 1.5 MPa. Although the hydrogen can be used in the indirect liquefaction process to increase the balance ratio, the large electrical power requirements and present day high capital cost - approximately 2.8 times the cryogenic capital cost - will probably limit its application to countries with low-cost hydro and nuclear generating capacity.

In pressure swing absorption (PSA) air is compressed to 400 kPa and passed through a packed bed of molecular sieves where oxygen and nitrogen are separated by utilizing the difference in molecular size of the two species. This process is preferred where plant capacities range from 9 to 36 t/d. Since these capacities are too low for the size of plants envisaged this route will be of limited value for oxygen gasification.

Development in membrane technology may provide another option for the generation of O_2. Membrane technology under development by Asahi Glass Co. (Tokyo, Japan) and UOP allows air enrichment to between 30% and 40% O_2. Asahi Glass Co.'s membrane is composed of a thin film (<0.1 µm) of fluoropolymer supported by a 50 µm layer of aromatic polymer and then reinforced with a 200 µm layer of cloth. A pressure differential of 70 kPa is sufficient to produce 40% O_2 enrichment when air is fed at atmospheric pressure (Anon, 1984a). UOP can produce 30% enrichment using a thin film of demethyl-silicone supported on porous polysalfone (Anon, 1984b).

5. SYNGAS CONDITIONING

It is evident that syngas produced by the gasification of biomass is not suitable for methanol production without further processing. Unit processes that are required are discussed below.

5.1 Particulate Removal

Ash and char can be removed with cyclones (Creusot-Loire, Lurgi, etc.) and possibly high temperature filters (MINO). To increase collection efficiencies, development work is continuing on the high temperature cleaning of hot gases using cyclones, electrostatic precipitators, granular-bed filters, and baghouses (Kohn, 1981). After removal the char is recycled back to the gasifier or used for the production of steam. Tar and oil can condense onto cold surfaces and cause operational problems; therefore, wet scrubbers and, if necessary, electrostatic precipitators are employed (Beenackers and Van Swaaij, 1983; SERI, 1980; Connor, 1982).

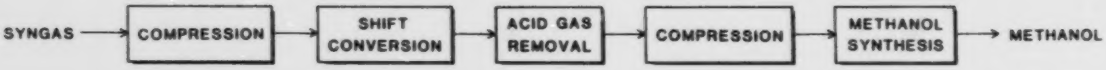
5.2 Reforming

Reforming includes both the production of methane by the catalytic cracking of higher paraffin hydrocarbons and its reaction with steam to produce CO and H_2. Steam reforming of methane is shown in equation [6].

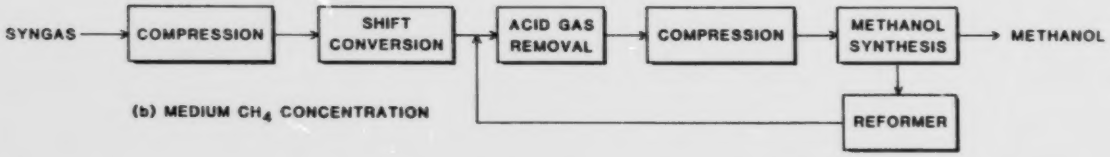
[6] $$CH_4 + H_2O = CO + 3H_2$$

The concentration of CH_4 in the syngas determines the need for reforming (Wan and Price, 1982b; Brandon et al., 1984; Bridgwater, 1984). It is not required for concentrations less than 3% since the methanol synthesis unit can accept this and a purge stream is sufficient to prevent accumulation of inerts in the circuit. For concentrations between 3 and 10% the methanol synthesis recycle stream must be reformed, while for higher concentrations it is the main syngas stream which must be reformed. Process flows for these conditions are shown in Figure 5.1 (Wan and Price, 1982b).

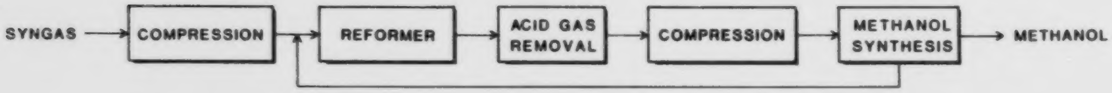
Methane is reformed with a catalyst that contains 16 to 20% Ni as NiO, supported on calcium aluminate, alumina, or calcium aluminum titanate (Kirk and Othmer, 1978). Since the conversion of methane is favoured thermodynamically by high temperatures and low pressures, the catalyst is usually packed into tubes and heated in a furnace. The exit gas temperature from the reformer is in the range of 800 to 900°C (SERI, 1980; Kirk and Othmer, 1978; Resource Planning Associates, 1982); however, the pressure is dependent upon the location of the reformer in the process circuit, and hence on the methane concentration in the syngas. A steam-to-carbon mole ratio in excess of three is used to prevent carbon formation (inverse of the



(a) LOW CH_4 CONCENTRATION



(b) MEDIUM CH_4 CONCENTRATION



(c) HIGH CH_4 CONCENTRATION

Figure 5.1. The effect of methane concentration on process configuration (based on Wan and Price (1982b)).

carbon-hydrogen and Boudouard reactions) and catalyst deactivation according to Kirk and Othmer (1978), but it is dependent upon gas composition and upstream processing. A ratio of 1.2 has been used in a design study reported by SERI (1980). With the temperatures, pressures, and steam ratios considered the product gas composition corresponds to a 15°C approach (lower) to equilibrium (Kirk and Othmer, 1978) and approximately 80% of the methane is converted (Earl, 1978). Reaction kinetics have been considered by Van Hook (1980).

The concentrations of sulphur and olefins in the syngas must be less than 0.1 ppm and 0.5%, respectively, due to the susceptibility of the reformer catalyst to poisoning (Smith and Wang, 1984) and are comparable with those required for methanol synthesis. High concentrations of olefins can be reduced by hydrogenation and have been discussed by Wan and Price (1982b) and SERI (1980).

Reforming is an energy intensive process and the heat duty of the reformer is equivalent to approximately 25% of the heating value of the feedstock. Flue gas temperatures from the furnace range from approximately 980 to 1040°C and process gas temperatures from 800 to 900°C, as mentioned above. Heat recovery is essential.

Syngas can be reformed autothermally by injecting oxygen into the gas, as practised by Creusot-Loire and MINO. The combustion of CO, H_2, and CH_4 provides heat for the reactions, but the production of CO_2 increases the acid gas removal requirements.

5.3 CO Shift

The quantity of hydrogen that is required to react with CO and CO_2 to produce methanol is such that the balance ratio should be in the range of 2.1 to 2.2. Due to the composition of the feedstock and the process conditions employed, this condition is not met by the syngas produced by the gasifier. To increase the concentration of hydrogen, the water gas shift reaction, given in equation [7], is used.

[7] $CO + H_2O = CO_2 + H_2$

Two types of catalysts, differing mainly in their activity and tolerance to various poisons, are used for this reaction (Newsome, 1980; Wan and Price, 1982a; Kirk and Othmer, 1978). These are the iron-based "high temperature" catalysts and the copper-based "low temperature" catalysts. The iron-based shift catalysts are employed in industrial shift converters at temperatures ranging from 300 to 450°C and pressures from atmospheric to 8.4 MPa. Syngas with CO concentrations from 3 to 80% can be processed by these catalysts. A typical composition of the iron-based catalyst is 74% Fe_2O_3, 10% Cr_2O_3, 0.2% MgO, and the remainder volatiles, reported in the unreduced state. Prior to use the Fe_2O_3 must be reduced to Fe_3O_4 in a reducing environment at temperatures of 250 to 400°C. The catalysts are unsupported and Cr_2O_3, the main additive, is believed to act as a stabilizer rather than a promoter and reduces high temperature sintering and surface area loss. The catalysts are tolerant to sulphur at concentrations up to 50 ppm, but chlorine can cause irreversible poisoning and only 1 ppm can be tolerated. Phosphorus, silicon compounds, and unsaturated hydrocarbons can also have adverse effects.

The copper-based shift catalysts are more active than the iron-based catalysts and are therefore used at temperatures ranging from 200 to 250°C, where the equilibrium is more favourable for the formation of hydrogen. This allows a lower steam-to-gas ratio, and hence reduced equipment size. It is also claimed that selectivity is improved. A typical catalyst composition, in the unreduced state, is 64% ZnO, 15% Cr_2O_3, 15% CuO, and the remainder, oxides of Mn, Al, and Mg. The ZnO and Cr_2O_3 act as structural stabilizers and promoters, and reduction is achieved in a reducing atmosphere at temperatures ranging from 200 to 250°C. These catalysts are very susceptible to poisoning by sulphur and chlorine and less than 0.1 ppm of the former can be tolerated in the syngas. Guard beds of ZnO are often employed to reduce the concentration of poisons.

Industrial reactors using these catalysts are generally operated adiabatically and temperature increases through the catalyst bed since the water gas shift reaction is exothermic at the temperatures used. A single stage reactor is employed where high purity hydrogen is not required, which would be the case for methanol synthesis.

5.4 Acid Gas Removal

Acid gas, which includes CO_2 and sulphur compounds such as H_2S, COS, and sometimes mercaptans, can be removed by a number of commercial systems based on solvent extraction, as discussed by Tennyson and Schaaf (1977), Mohr and Ranke (1984), and Kirk and Othmer (1978). Depending upon the solvent, acid gas can be removed by chemical or physical processes, or a combination of the two. Acid gas present in the feed at low or intermediate partial pressures (generally less than 0.5 to 0.7 MPa) can be removed by chemical solvents, while physical solvents are effective at high partial pressures (generally above this range). Although the regeneration of chemical solvents requires substantial heat, acid gas partial pressures are expected to be relatively low based on projected gasifier operating pressures (0.1 to 1.1 MPa) and syngas compositions (10 to 30 mol%), therefore this type of solvent will likely be the one of choice.

Chemical solvents include a number of chemicals and processes. One of the first chemical solvents was monoethanolamine (MEA) which was developed in the 1920s and which is still used today for the removal of CO_2 (Girbotol Amine process developed by the Girdler Corp.). Due to corrosion problems dilute aqueous solutions (15 to 20 wt.%) are normally used; however, addition of corrosion inhibitors allows the concentration to be increased to over 30% (Amine Guard developed by Union Carbide (Kosseim et al., 1984). This allows a reduction in the recirculation rate, hence a reduction in the equipment capital costs. Irreversible reaction with contaminants such as COS and CS_2 can result in permanent degradation of the MEA and would normally require diethanolamine (DEA) to be used in its place; however, the concentration of these contaminants is expected to be low for biomass gasification. Other amines such as diglycolamine (DGA), triethanolamine (TEA), and diisopropanolamine (DIPA, ADIP) are also in use. The Econamine process by Fluor uses DGA, while Shell's Sulfinol process uses a mixture of physical and chemical solvents - sulfolane and diisopropylamine (usually). Amines are very effective at removing acid gas when it is present at low partial pressures (generally 70 to 100 kPa) in the feed gas. In the absence of H_2S, the CO_2 partial pressure of the treated gas can be reduced to 0.03 kPa. This far exceeds the requirements for methanol synthesis.

Potassium carbonate is another chemical solvent; however, low rates of absorption prevented its commercialization until the 1960s when hot activated processes were developed. Activation, achieved by the use of additives which are described as promoters, activators, or catalysts, increased the absorption and desorption rates, improved removal efficiency, and reduced energy requirements. Corrosion inhibitors are used as well. The additives used in the Benefield (licensed by Union Carbide (Bartoo, 1984) and Catacarb processes are proprietary; however, boric acid, glycine, or arsenic trioxide are used by the Vetrocoke process. Although arsenic trioxide is the most effective in the latter process, there is some resistance to its use. DEA is also added to the carbonate solution in the Benefield process, but it is not considered to be an additive. Advantages of hot activated potassium carbonate, compared with amines, are its higher operating temperature and lower heat requirements for regeneration, but higher acid gas partial pressures are required for its operation. Partial pressure requirements range from those for the amines to 0.5 to 0.7 MPa. Although COS and CS_2 do not adversely affect this solvent, SO_2 and SO_3 can react irreversibly with it. This should not pose a problem with syngas derived from biomass gasification due to the low levels of sulphur present.

Since methanol catalyst is very susceptible to sulphur poisoning a ZnO guard bed is usually considered prior to synthesis. If acetylene is also present then an activated carbon bed is required prior to the ZnO bed because the latter causes polymerization of the acetylene at temperatures between 260 and 370°C (SERI, 1980).

6. ECONOMIC ASSESSMENT

Since the gas processing steps envisaged for the indirect liquefaction of biomass are well established in the chemical industry and the pretreatment operations have been used in the forestry industry, the greatest uncertainty in methanol production cost will be caused by the gasifier. This uncertainty will be the result of two factors: the operating variability of a gasifier in an established commercial plant, which has yet to be built, and the accuracy with which results from small scale gasifiers can be extrapolated to commercial size units. To obtain an estimate of the methanol cost, a simple mathematical model was developed for the indirect liquefaction process and a probability function for the supply price of methanol determined for a particular gasifier using published operating data. The difficulty with this approach is the limited availability of data for some gasifiers or the wide range in operating conditions which would not normally be encountered in a commercial unit, and the uncertainty associated with scale-up.

The model, shown in Figure 6.1, determines the supply price of methanol given the characteristics of the biomass, the composition of the syngas, the yield of char produced by the gasifier, and the methanol production rate. Equilibrium models are used for both the reformer and the methanol reactor, which are operated at 850°C and 2 MPa, and 250°C and 5 MPa, respectively. The input of steam and oxygen to the gasifier is determined from a mass and heat balance. The concentration of CH_4 at the outlet of the reformer is set at 1% and the balance ratio and CO_2 concentration at the inlet of the methanol reactor are set at 2.1 and 4%, respectively. A purge stream from the methanol synthesis unit is directed to the inlet of the reformer to prevent excessive build-up of methane in the recycle stream in the methanol unit. Char produced by the gasifier and wood, if necessary, is fed to a boiler which produces power for compression of the feed and recycle streams in the methanol synthesis unit, and for the cryogenic oxygen plant. Steam is also produced for the gasifier, should it be

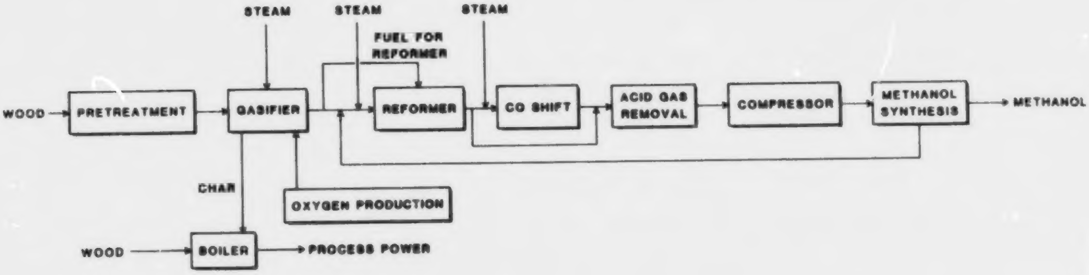


Figure 6.1. Process configuration for the indirect liquefaction of wood simulation.

required. It is assumed that there will be no difficulties in using the char in a boiler, but it must be recognized that char produced by a gasifier has been devolatized and a fluidized bed is the most appropriate combustor (Feldman et al., 1983).

An exponential relationship between the process unit capital cost and the capacity, cost = a × $(\text{capacity})^b$, was developed for each process unit using data from the literature (Moffatt and Anand, 1984; Fishkind, 1982; Wham et al., 1981; Buckingham et al., 1981; Wan and Price, 1982a; Corneil et al., 1977; Simons Resource Consultants and B.H. Levelton & Associates Ltd., 1984). Process unit capital costs in terms of flow rate or conversion are given in Table 6.1. Although the cost relationship used is in general too simplistic since cost is a function of a number of parameters such as flow, composition, temperature, and pressure, it is considered satisfactory for the present level of development of the model and the large variation among costs quoted in the literature. The cost of utilities, building and site development for a plant producing 500 t/d of methanol is given in Table 6.2 and has been based on Wan and Price (1982a).

The battery limit capital cost (BLCC) is the sum of the process unit capital costs, with the exception of the boiler, as given in Table 6.1; and the offsite capital cost is the sum of the utilities, boiler, buildings, and site costs. The total plant capital investment is the sum of the battery limit and offsite capital costs.

The total annual operation and maintenance cost is composed of the raw material, purchased utilities, labour, and capital related costs, and is based on 8000 h of operation per year. The raw material costs include those for wood, chemicals, and catalysts; and the utility costs are for power, cooling water, and process water. Labour consists of direct labour, supervision, and overhead. Supervision is 25% of the direct labour cost and overhead is equivalent to the sum of the direct and supervision labour costs. The capital related costs are for maintenance, at 4% of the BLCC, and general plant overhead, at 2.6% of the BLCC.

The chemical, catalyst, and labour costs, based on the data in Wan and Price (1982a) and Moffatt and Anand (1984), are given in Table 6.3 for various gasifiers. The chemical and catalyst costs have been updated to January 1985 using the Chemical Week index of industrial chemical prices. Labour requirements are taken directly from the publications cited above, and direct labour costs are based on a wage rate of $12.40/h and a 33% payroll burden.

The total plant capital investment, annual operating and maintenance costs, and the latter, but excluding feedstock costs, are given in Table 6.4 for the gasifiers considered.

Table 6.1. Process unit capital costs

Process unit	Cost[1] $(Can) 1985		Capacity		Reference	Comments
	a	b	Units	Range		
Wood preparation & storage	11621	0.555	kg(dry)/h	2.5×10^4- 9.4×10^4	Moffatt and Anand (1984)	Assume small variation among gasifiers Not suitable for Koppers-Totzek
Gasification	5834	0.744	kg(dry)/h	2.5×10^4- 9.4×10^4	Moffatt and Anand (1984)	Molten Salt
	852	0.885	kg(dry)/h	3.7×10^4- 3.9×10^4	Wan and Price (1982a)	SERI
	119	1.101	kg(dry)/h	3.1×10^4- 4.4×10^4	Wan and Price (1982a)	PNL
	2468	0.800	kg(dry)/h	4.5×10^4- 6.0×10^4	Wan and Price (1982a)	BCL
	9149	0.635	kg(dry)/h	4.5×10^4- 6.0×10^4	Wan and Price (1982a)	Fluidized Bed: based on BCL data
Oxygen production	35370	0.634	kg O2/h	1.0×10^4- 1.7×10^4	Wan and Price (1982a)	Significant variations in cost in literature
Reformer	745	0.628	gmol/h of CH_4 converted	8.9×10^4- 2.6×10^5	Wan and Price (1982a)	Poor comparison with Wham (1981) could be due to extrapolation

Table 6.1 (Cont'd).

Process unit	Cost* $(Can) 1985		Capacity		Reference	Comments
	a	b	Units	Range		
CO shift	30000	0.42	gmol/h of CO converted	4.5×10^4- 1.7×10^5	Moffatt and Anand (1984)	Significant variations in costs quoted in literature
Acid gas removal	5453	0.551	gmol/h of CO2 removed	3.2×10^4- 1.2×10^5	Moffatt and Anand (1984)	Significant variations in costs quoted in literature
Compression	4.77	0.614	cal/h	1.4×10^8- 5.4×10^9	Moffatt and Anand (1984)	Compression requirements estimated using simulation model Significant variations in costs quoted in literature
Methanol synthesis & purification	1.915×10^6	0.451	t/d of CH_3OH	267- 1000	Moffatt and Anand (1984)	Good consistency in costs quoted in literature
Boiler	2.26×10^6	0.33	kg/of 4.2 MPa steam	32.3- 60.4	Simons Resource Consultants and B.H. Levelton & Associates Ltd. (1984)	Major variations in capital costs, based on process variations

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[1] Cost = a × Capacity^b

Table 6.2. Offsite capital costs for a 500 t/d methanol facility

	Capital cost M$ CAN, Jan. 1985
Raw water treatment and cooling tower	2.74
Utility distribution	0.69
Waste water treatment	2.4
Building and site development	2.06

Table 6.3. Operating costs for a 500 t/d methanol facility

Gasifier	Purchased utilities $/t of dry wood (CAN, Jan. 1985)	Direct labour $/t of dry wood (CAN, Jan. 1985)
Molten salt	5.6	4.9
SERI	5.1	5.6
PNL	16.0	5.3
BCL	8.5	4.0
Fluidized bed	8.5	4.0

Table 6.4. Total plant capital investment and operating and maintenance costs for a biomass-to-methanol plant (500 t/d) using various types of gasifiers

		Levelized annual operating and maintenance costs[1-3]	
Gasifier	Total plant capital investment[1]	Total	Excluding feedstock
SERI	102.0 (1.8)	21.5 (0.8)	12.4 (0.8)
Fluidized bed	104.9 (0.7)	20.5 (0.6)	11.4 (0.3)
PNL	81.2 (6.7)	24.3 (1.5)	14.6 (1.0)
BCL	99.4 (5.9)	32.5 (7.6)	16.5 (3.4)
Molten salt	109.1 (4.7)	25.6 (2.6)	13.7 (1.2)

[1] $CAN, Jan. 1985, standard deviation in parentheses.

[2] Discount factor of 7%/a.

[3] Plant life of 20 years.

The levelized supply price of methanol is determined using equation [8] (Overend, 1982).

$$[8] \qquad P_s = \frac{\sum_{t=0}^{n} C_t/(1 + i)^t + \sum_{t=0}^{n} O_t/(1 + i)^t}{\sum_{t=0}^{n} Q_t/(1 + i)^t}$$

where

P_s = supply price
C_t = capital cost in year t
O_t = operating and manufacturing cost in year t
Q_t = production in year t
i = discount factor
n = project life, years

In this analysis a one-year construction period is assumed and production rates (500 t/d of methanol) and operating costs are constant. The project life is 20 years, including one year for construction, and the discount factor is 7% which is considered the social value of the project (Summer et al., 1984). Taxes and inflation are not included since the analysis is used for comparison purposes only.

The supply price was determined using gas compositions and associated char yields for various experiments reported in the literature for the SERI, INCO (oxygen fluidized bed), PNL, BCL, and Molten Salt gasifiers. Its probability function was fitted to a Gaussian curve and two supply prices were then determined such that 25% and 95% of the measured values were less than these prices. The results, as a function of the wood cost, are shown for the various gasifiers in Figures 6.2 to 6.6.

The results for oxygen gasification with the SERI stratified downdraft gasifier (0.9 t/d) are given in Figure 6.2 and are based on the data from Reed et al. (1982) for atmospheric pressure operation. A char yield of 0.5% was used for the six test runs considered. The small variation in the methanol supply price for a given wood cost is a reflection of the relatively uniform syngas composition. It should be cautioned that a commercial gasifier may not produce this quality or yield of gas since scale-up and operating considerations may dominate.

Data generated by the INCO gasifier (0.6-3.0 t/d (Inco Metals Company, 1980)) were used to determine the methanol supply price for fluidized bed,

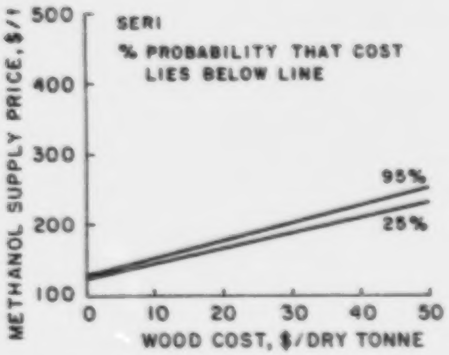

Figure 6.2. The effect of wood cost on the methanol supply price for the SERI gasifier.

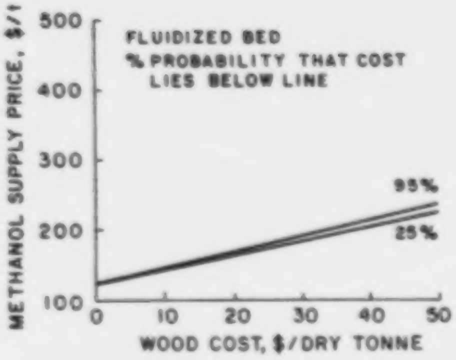

Figure 6.3. The effect of wood cost on the methanol supply price for the fluidized bed gasifier.

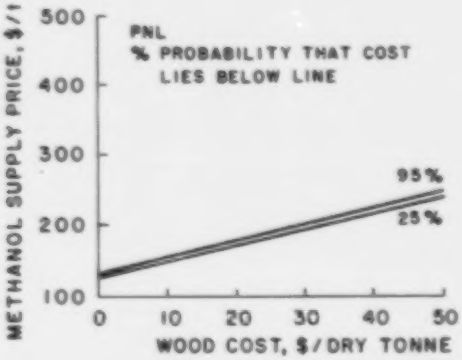

Figure 6.4. The effect of wood cost on the methanol supply price for the Battelle Pacific Northwest Laboratory gasifier.

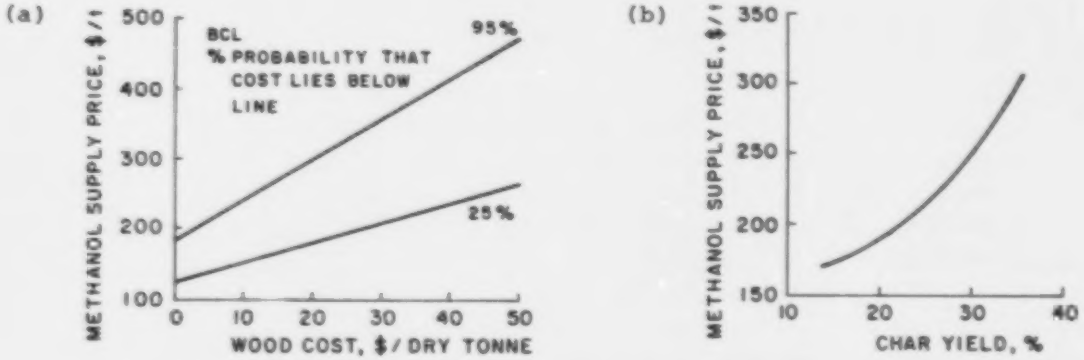

Figure 6.5. (a) The effect of wood cost on methanol supply price for the Battelle Columbus gasifier; (b) the effect of char yield on methanol supply price for the Battelle Columbus gasifier.

oxygen gasification. A mean char yield was determined from a continuous test and two batch tests, and the standard deviation was determined from 12 other batch tests. An average gas composition was used in the analysis since there was little variation among tests. The results are given in Figure 6.3.

The methanol supply price for the PNL catalytic steam gasifier was determined using data from six test runs of a bench scale, dual vessel gasifier (0.7-1.0 kg/h (Brown, 1985)). The first vessel was the primary gasifier and the second a catalytic reactor. The syngas composition and the associated char yield, determined from that composition for both a stationary and a fluidized bed catalytic reactor, were used in the cost calculations. Since the simulation model does not include a hydrogenation module, the gas composition was adjusted by assuming hydrocarbons were converted to methane in the gasifier. Also the model does not take into consideration the energy requirements for steam fluidization. The supply price is given in Figure 6.4 as a function of the wood cost. The small variability in the supply price is in part due to the limited duration of the test runs for the fixed catalytic reactor. The effects of significant catalyst deactivation which occurred after 10 to 12 h of operation were not included in the results. Severe catalyst deactivation also occurred in a 0.9 t/d process research unit which utilized a fixed catalytic reactor. The success of this approach will therefore depend upon stabilization of the catalyst activity.

The BCL steam gasifier produces high char yields and a syngas which is not particularily suitable for methanol production because of the high concentrations of hydrocarbons. However, the methanol supply price has been estimated using operating data given by Feldman et al. (1983). Twelve test runs with dry wood feed rates ranging from 1.2 to 2.0 t/d and gasifier temperatures between 788 and 840°C were used in the analysis. Using the same assumptions as with the PNL gasifier resulted in methanol supply prices as shown in Figure 6.5a.

The methanol supply price for molten salt gasification was estimated using the syngas compositions and yields given by Moffatt and co-workers (1982, 1984) for combined steam and oxygen gasification (seven test runs). All carbon conversions to gas were reduced so that the maximum conversion obtained in the experiments did not exceed 100%. The methanol supply price was then determined for each test run using the gas composition reported and the associated char yield. The supply price, as a function of the wood cost, is shown in Figure 6.6.

Comparing the methanol supply price for the various gasifiers indicates there is little difference for the SERI, Fluidized Bed, PNL, and

Molten Salt designs. The methanol supply price for the BCL gasifier is also comparable to that of the others at the 25% probability level; however, substantially greater variability is evident. This gasifier is probably the least suited of those considered for the synthesis of methanol.

Since the methanol supply price is relatively insensitive to the type of gasifier employed, substantial reduction in methanol supply price is unlikely to result from further work in this area. Because all unit processes are established individually, it is unlikely that the methanol supply price will be reduced significantly using this feedstock.

The cost of producing methanol by indirect liquefaction of biomass has been assessed by a number of authors, but varying assumptions result in different costs and comparison between authors must be done cautiously. The insensitivity of methanol supply price to gasifier design was also found by Wan (1982). In that study the variation in methanol production cost was less than 15% for the PNL, SERI, Koppers-Totzek, and Winkler gasifiers and was considered to be insignificant in light of the uncertainty in the available data and the assumptions employed. The results are given in Table 6.5. Resource Planning Associates (1982) estimated the potential capital reduction for a Koppers-Totzek based process. The potential cost reduction was greatest for the gasifier, 13.4%, and least for the CO shift and acid gas removal units, 1.7%. The total potential reduction was given as approximately 40%, but this failed to recognize that cost saving measures applied to one unit could have deleterious effects on another unit and the total savings would not be the sum of the unit potential savings (see Bridgwater (1984)). The results are also based on data which were available prior to 1979. The sensitivity of the methanol production cost to the CH_4 concentration for a given CO_2 concentration and H_2/CO ratio is shown in Figure 6.7 and has been considered in detail by Bridgwater and

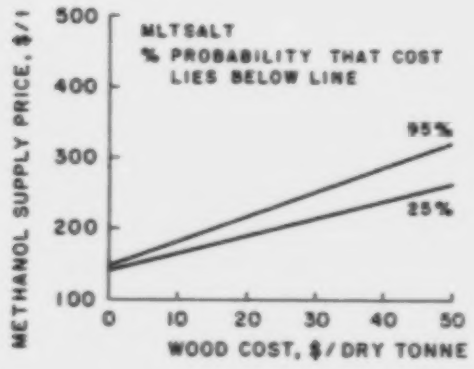

Figure 6.6. The effect of wood cost on the methanol supply price for the molten salt gasifier.

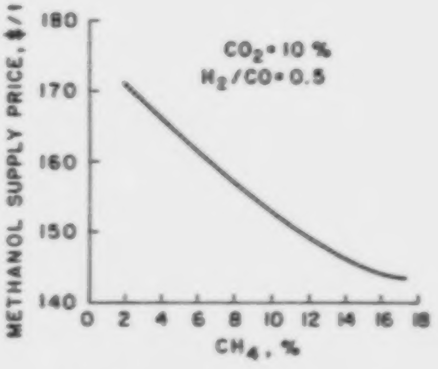

Figure 6.7. The effect of CH_4 concentration on methanol supply price (fluidized bed gasification).

Table 6.5. Comparison in conceptional biomass to methanol processes (Wan, 1982)

	PNL	SERI	Winkler	TOTZEK
Carbon conversion to gas, %	100	100	100	100
H_2/CO	1.81	.52	.81	1.12
CO/CO_2	1.28	3.53	2.32	1.52
Dry gas yield, m^3/kg of dry wood	1.71	1.40	1.06	1.52
Carbon conversion to methanol,[1] %	32.4	24.6	28.6	26.7
Thermal conversion to methanol, %	50.2	39.9	44.4	42.3
Total plant capital costs[2] M$ US, 1981	79	94.4	99.6	106.1
Annual operating & maintenance costs[3] M$ US, 1981	20.7	23.3	22.6	23.5
Total methanol production costs[4] $ US 1981/l	0.22	0.25	0.26	0.27

[1] Based on HHV of feedstock and products.

[2] 450 t/d.

[3] Operating costs include feedstock (wood) at $25/T(dry).

[4] Private financing-100% equity capital, 20-year-life, 12% DCF, 48% tax, 16 year sum of digits depreciation.

Shand (1983). The production cost decreases as the methane concentration increases thus indicating the cost effectiveness of reforming. This also suggests that the actual quality of the syngas is less important than the yield.

The sensitivity of the methanol supply price to the char yield is shown in Figure 6.5b for the BCL gasifier. As the char yield increases from 14% to 36%, the methanol supply price increases by 78%. Therefore, in light of the cost effectiveness of reforming, as shown above, one of the primary considerations in gasifier design and operation is syngas yield, which should be maximized. The composition may be suitably altered by downstream processing.

The scale of production, considered previously by Overend (1982), Mudge et al. (1981a, b) and Brown et al. (1983), can have a significant impact upon the methanol production cost as shown in Figure 6.8 for methanol production rates of 500, 1000, and 2000 t/d and for wood costs between $0 and $50/t. The mean cost was estimated for oxygen, fluidized bed gasification using the previously described model. In general, the methanol supply price varies inversely as a fractional power of the plant capacity. The optimum scale of production has been examined by Eggers et al. (1982); however, feedstock requirements may be a constraint because of the land area requirements - Fishkind (1982) found that a 900 t/d methanol plant located in central Florida would require a 28 kha eucalyptus energy plantation. Brandon et al. (1984) estimated that the maximum scale would be approximately 500 t/d of methanol.

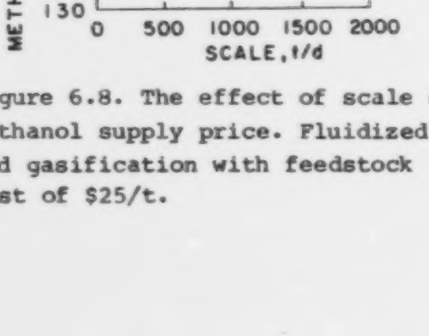

Figure 6.8. The effect of scale on methanol supply price. Fluidized bed gasification with feedstock cost of $25/t.

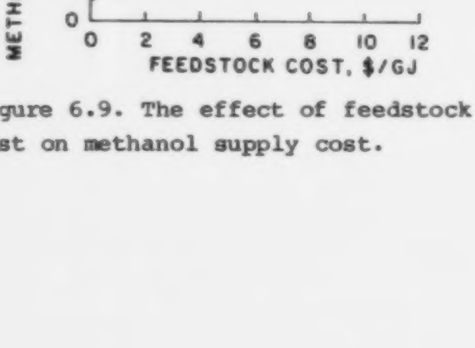

Figure 6.9. The effect of feedstock cost on methanol supply cost.

Since natural gas and coal may also be used as feedstocks, as discussed above, it is valuable to compare the supply price of methanol when derived from these feedstocks with that from biomass. The supply prices for fluidized bed gasification of biomass, for entrained bed (Texco) gasification of coal, and for steam reforming of natural gas are shown in Figure 6.9. The cost for natural gas and coal derived methanol is based on the data given by Stratton et al. (1982) and Buckingham et al. (1981). Operating and capital costs have been adjusted so that the same simplifying assumptions apply in these cases as to the biomass case. Although the supply cost of methanol appears to be more sensitive to feedstock cost for biomass than for coal, biomass is competitive with coal. However, neither of these feedstocks are currently competitive with natural gas. For biomass and coal feedstocks to be competitive with natural gas the cost of the latter would have to exceed $4/GJ while the former would have to be valued at $1 to $2/GJ. Relaxing some of the simplifying assumptions would tend to increase this difference.

7. CONCLUSIONS

The production of methanol from biomass is technically feasible, but further research and development is required for the gasifier because of the current scale of operation and limited availability of operating data. Due to these factors the gasifier represents the area of greatest technical risk. Based on the simulation model, established gas processes such as reforming are cost effective; therefore research objectives should focus on maximizing syngas yield. The operating characteristics of the gasifier will also be of concern in this regard.

The cost of producing methanol from biomass appears to be comparable with that from coal. However, biomass is the favoured feedstock due to the reduced financial risks. Since the cost of producing methanol from natural gas is significantly less, biomass will not be considered as a suitable substitute until a substantial price differential develops between the two feedstocks. Significant reductions are not expected in the methanol supply price when using biomass since it is relatively insensitive to the type of gasifier employed and the other process units are well established industrially. Further research in gasification is unlikely to make a significant financial difference.

With respect to the gasifier, allothermal steam gasification appears to be economically the least favourable for the synthesis of methanol. The syngas yield is low and the high concentrations of hydrocarbons increase gas treatment costs. Although catalysts improve the gas composition they are subject to deactivation and do not substantially improve the economics relative to autothermal gasification. Improved fluidized bed gasifier operability due to the lower temperatures would be the motivation for continuing with this approach.

Fixed bed gasifiers suffer from solids flow problems, poor syngas yield and quality (tars and oils in the counter-current), and scale-up difficulties (co-current). Although these types of gasifiers can result in a methanol supply price which is not significantly different from the other gasifiers, they will probable have little impact due to these operating characteristics.

Entrained bed gasifiers may require excessive feedstock preparation, and may have dynamic control problems due to the short residence times and feeding difficulties (especially under pressurized operation). Since operating data are practically nonexistent they cannot be totally excluded from further consideration at this stage.

Molten salt gasifiers may produce an improved syngas quality due to the catalytic action of the molten salt and greater operational flexibility with respect to feedstock quality. The methanol supply price is not substantially different from other gasifiers, therefore its feasibility may depend upon material considerations such as corrosion. Further data are required to assess this approach.

Autothermal, fluidized bed gasification appears to offer the greatest potential for the production of methanol by indirect liquefaction in the near future.

Development of the three-phase process of Chem Systems for the synthesis of methanol will result in higher conversion efficiencies and could result in greater flexibility with respect to the balance ratio. The latter could be particularily important for biomass gasification, which produces a low H_2/CO ratio, if a portion of the CO-rich unreacted gas can be used for other purposes. Also, the production of a mixture of methanol and higher alcohols using either this process or the more conventional processes would be favourable since gas processing requirements would be reduced and the alcohol fuel would be more compatible with gasoline for blending.

Gas cleaning costs will be lower with biomass than with coal due to the lower concentrations of catalyst poisons, such as sulphur and chlorine.

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APPENDIX A.

DESCRIPTION OF THE PROCESS SIMULATION MODEL

The model was written in Basic 3.0 for the Hewlett-Packard series 9000 computer and has a pyramidal structure. At the top of the pyramid is the data input statements which are described below under "Main Programme". This is immediately followed by the subprogramme "Process-logic" which calls a series of subprogrammes that conduct heat and mass balances on various process units that have been incorporated into a process sequence. The following is a brief description of the data input requirements and the subprogrammes.

A1. MAIN PROGRAMME

The main programme establishes both the dimensions of the variables and the COM blocks which are required, as well as the data that must be input. The latter requirement is given below.

(i) Wood characteristics: The proximate analysis of the wood is required as well as the higher heating value.

(ii) Gasifier: The type of gasifier, such as the Molten Salt (Mltsalt), SERI (Seri), PNL (Pnl), BCL (Bcl), or Fluidized Bed (Fluid bed), is specified, as well as the flow rate and composition of the syngas. Under normal operation the flow is set equal to unity. The yield of char must also be given. The temperature of the syngas and steam fed to the gasifier, in addition to the moisture content of the wood feed, are also required.

(iii) Reformer: The temperature of both the synthesis gas feed and the reformer (equilibrium temperature for the reforming of methane and the water gas shift reaction) are required. It has been assumed in this programme that the equilibrium temperatures of the two reactions considered are identical; however, it should be noted that this is not the case in practice and that the model could be improved. The pressure of the reformer must be specified as well as the stack gas oxygen concentration for the furnace. It is assumed in this simulation that a portion of the syngas is used to fire the reformer furnace. The equilibrium coefficient for the steam reforming of methane is also required. It is assumed that the activity coefficients for the species involved in this reaction are unity. Finally, the methane concentration in the outlet to the reformer must be specified.

(iv) CO-Shift: The temperature and pressure for the water gas shift reaction are required. An equilibrium coefficient for the inverse of the water gas shift reaction but formed using the activity coefficients in place of the concentrations is also required.

(v) Acid Gas Removal: The concentration of carbon dioxide and water in the outlet stream and the outlet temperature must be specified.

(vi) Methanol Synthesis: The temperature (equilibrium for the CO conversion and the water gas shift reactions) and pressure of the reactor and the equilibrium coefficients formed using the activity coefficients in place of the concentrations are required for the two reactions involved. The molar ratio of the recycle to feed flows must also be input. The programme can be operated so that either this ratio or the concentration of inerts (methane) in the recycle are held constant. Finally, the methanol production rate is required.

(vii) Wood Feed Dryer: The dryer is operated by burning a portion of the dry wood which it produces. The stack temperature and oxygen concentration are required as input.

(viii) Boiler: The boiler produces steam for the gasifier and power for compression-syngas, recycle gas, and oxygen generation. The temperature of the steam produced by the boiler and fed to the turbine as well as the temperature of the steam exiting the turbine must be input. The efficiency of the turbine is also required.

(ix) Economics: The project life and discount factor are required.

(x) Thermodynamic Data: Coefficients for determining the specific heats of the various species are required, as well as the heats and free energy of formation, and the critical constants.

A2. PROCESS-LOGIC

This subprogramme defines the sequence of process units that are required in the indirect liquefaction process. The sequence used is shown in Figures A1 and A2. The programme first checks that the mass balance is satisfactory for the gasifier, given the syngas composition and the wood composition and heating value. An inconsistency will terminate the run. Mass balances are then conducted on the process units used in the gas processing. Since a purge stream is recycled from the methanol synthesis unit back to the inlet of the reformer, an iterative procedure is used. Convergence is assumed to be satisfactory in the present analysis when there is less than 1% change in the methane recycle rate. The limiting conditions for the process units are discussed under the appropriate subprogrammes.

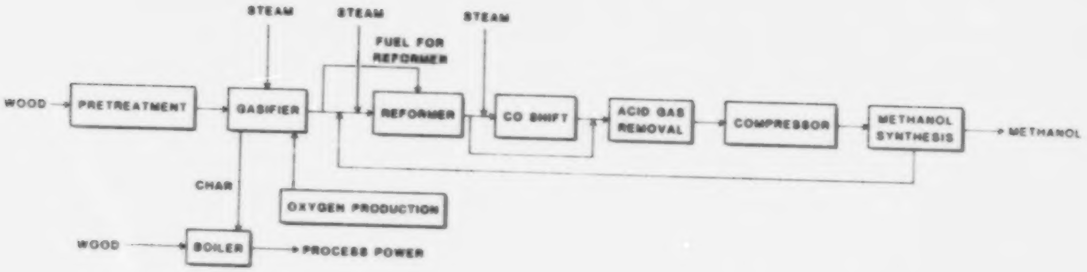

Figure A1. Process configuration for the indirect liquefaction of wood simulation.

After the mass balance for the downstream processing of the syngas is determined, a heat balance is conducted on the reformer to find the quantity of syngas which must be used in the furnace. The quantity of syngas required by the gasifier may then be determined and a heat and mass balance on the gasifier allows the determination of the wood feed required for gasification. The only pretreatment considered is drying, and the wood feed rate to the process is found from a heat and mass balance on the dryer.

The oxygen production requirements were determined by the mass and heat balance on the gasifier and the power requirements are based on the data given by Moffatt and Anand (1984). Compression requirements are determined for the syngas and for the recycle stream in the methanol synthesis process unit. The total power requirements are then determined and used in the boiler calculation.

Char produced by the gasifier is burned in the boiler to produce steam for the gasification and power as indicated above. If the boiler fuel requirements cannot be met by the char then wet wood is also fed to the boiler. The carbon conversion and the thermal (first law) efficiency for the process are then calculated.

The total plant capital and maintenance costs are determined given the rate of production of methanol, and the methanol supply price determined by an economic analysis.

A3. REFORMER

A3.1 Reformer(Yo(*),Fo)

Figure 3A is a schematic diagram of the process flow for the reformer. The reformer subprogramme determines product flow and composition given the syngas flow and composition and the desired concentration of methane in the outlet. A Newton-Raphson iterative procedure is used to determine the quantity of steam which must be input. Convergence is considered

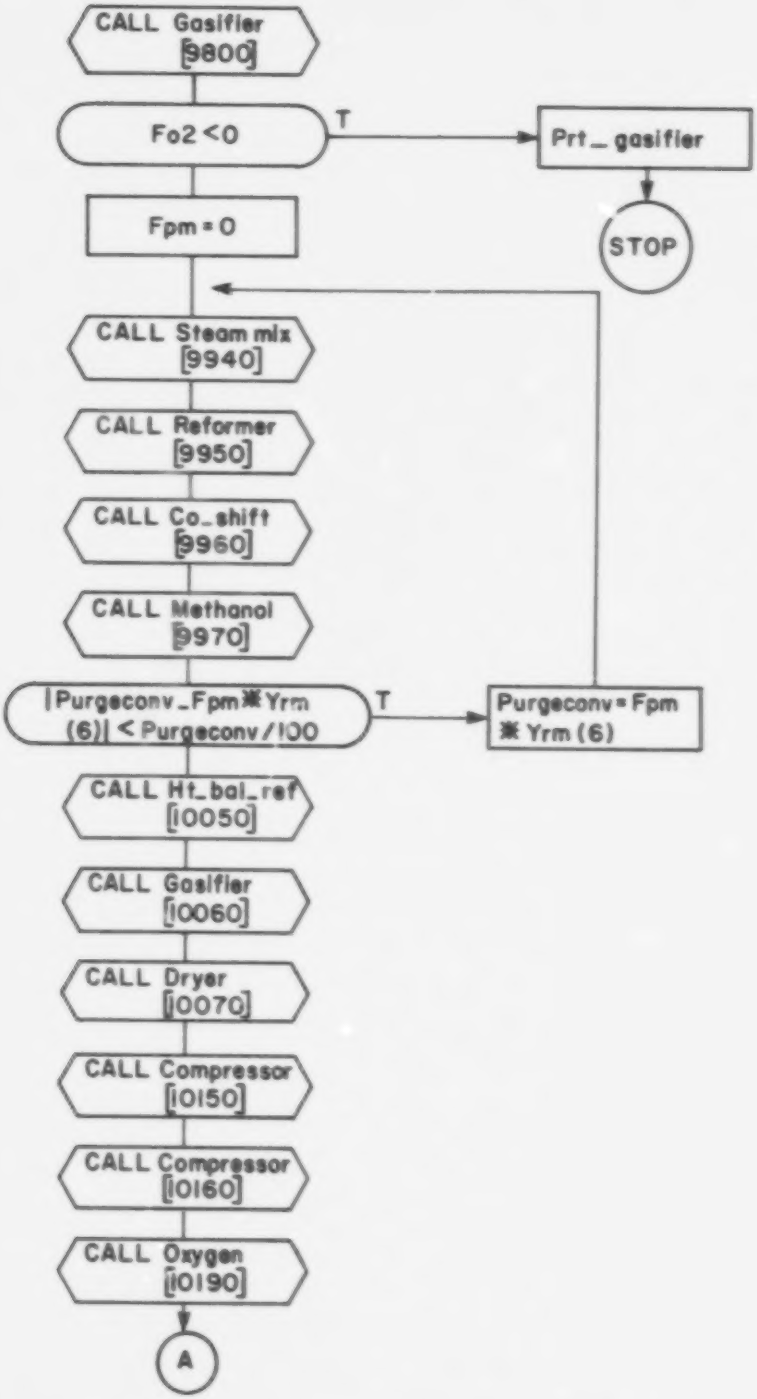

Figure A2. Flow chart for subprogramme "Process_logic." [], line number in programme listing.

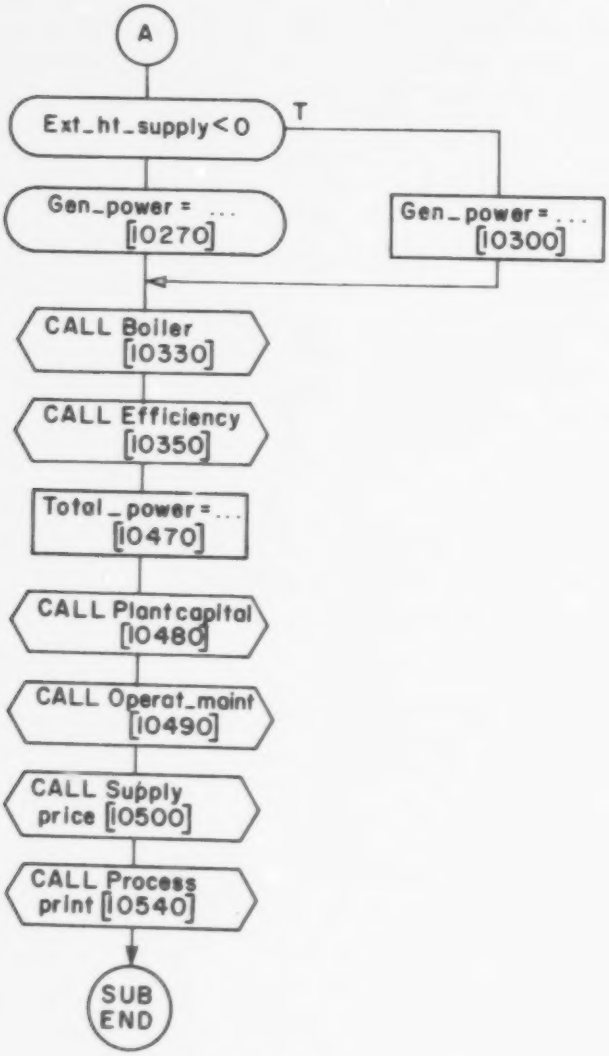

Figure A2. (Concluded)

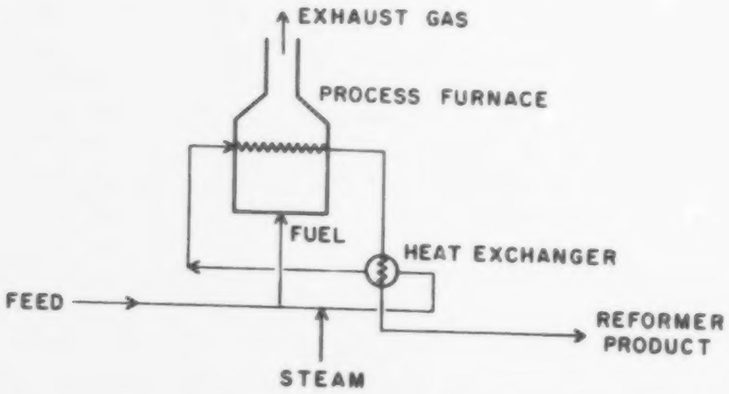

Figure A3. Process schematic of reformer.

satisfactory if the concentration of methane is within 10% of the target value, which is normally considered to be 1%. A process flow chart for the subprogramme is shown in Figure A4 and the nomenclature used is given in Table A1.

A3.1.1 Equilibriumr(Yo(*),Fo)

This subprogramme determines the equilibrium composition for a given feed composition, temperature, and pressure. Two reactions are considered in the calculation: the steam reforming of methane and the inverse water gas shift reaction, as illustrated below.

[A1] $CH_4 + H_2O = CO + 3H_2$

[A2] $CO_2 + H_2 = CO + H_2O$

In the programme X is defined as the conversion of CH_4 in reaction [A1] and Y is defined as the conversion of CO_2 in reaction [A2]. The equilibrium constant, K1, for reaction [A1] has been input as data at the start of the run while the equilibrium constant, K2, for reaction [A2] is calculated in the subprogramme Kshift.

The value of X is determined by using a crude iterative procedure. A value of X approaching the maximum value possible is first assumed and a corresponding Y determined using subprogamme "Recursion." The equilibrium constant for equation [A1] is calculated using X and Y; and the difference

Table A1 Nomenclature for the Subprogramme "Reformer"

Species :
CO : 1
CO_2 : 2
CH_3OH : 3
H_2 : 4
H_2O : 5
CH_4 : 6
N_2 : 7
O_2 : 8
Fo : molar flow rate of stream to be processed by unit
Ffr : molar flow rate of output stream
Methane : target methane concentration in outlet stream
Pr : reformer pressure, atm.
Steam : molar flow rate of steam
Tr1 : reformer temperature, °C.
Yfr(i) : molar concentration of component "i" in product stream
Yinr(i) : molar concentration of component "i" in feed to reactor
Yo(i) : molar concentration of component "i" in feed to unit

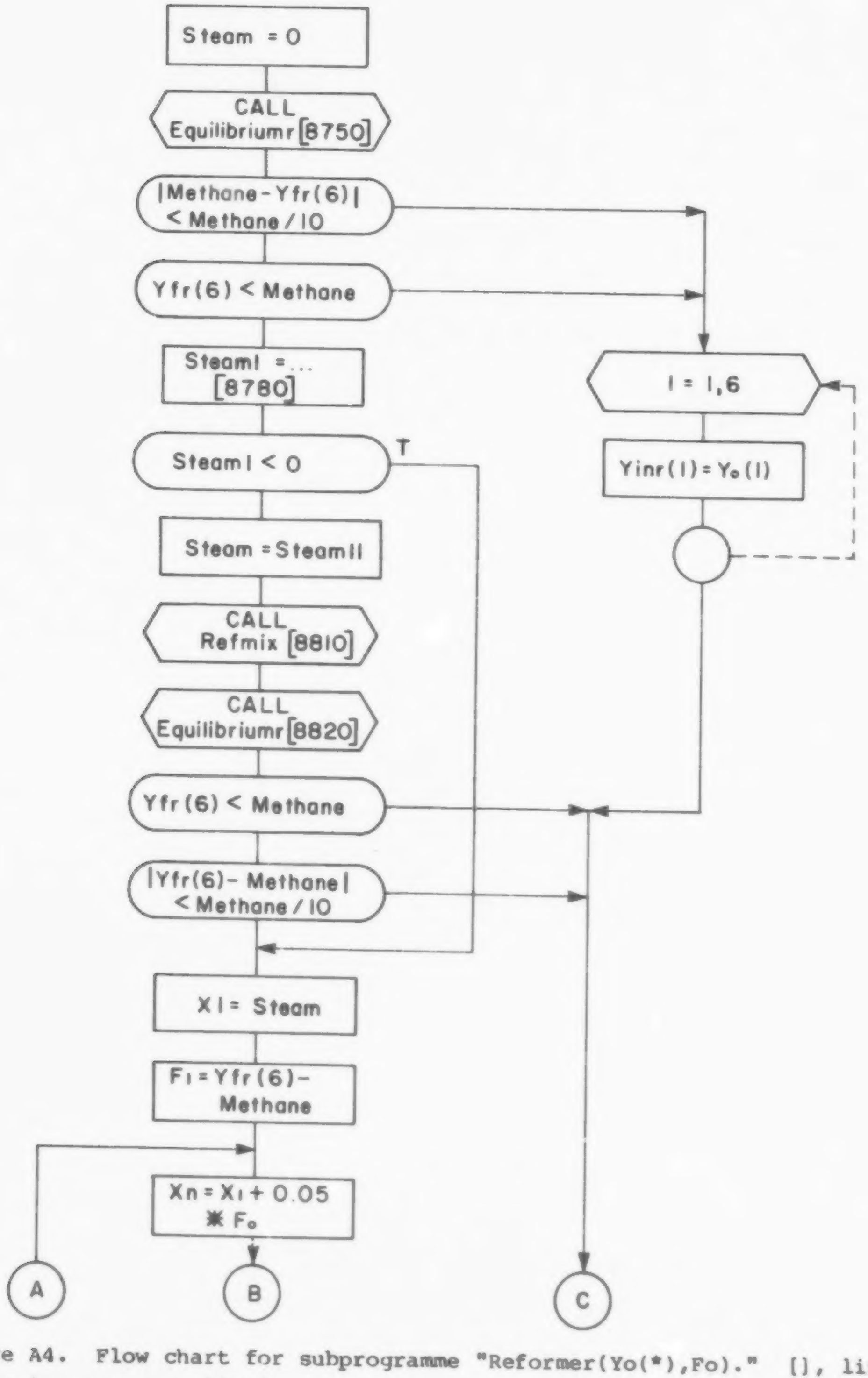

Figure A4. Flow chart for subprogramme "Reformer(Yo(*),Fo)." [], line number in programme listing.

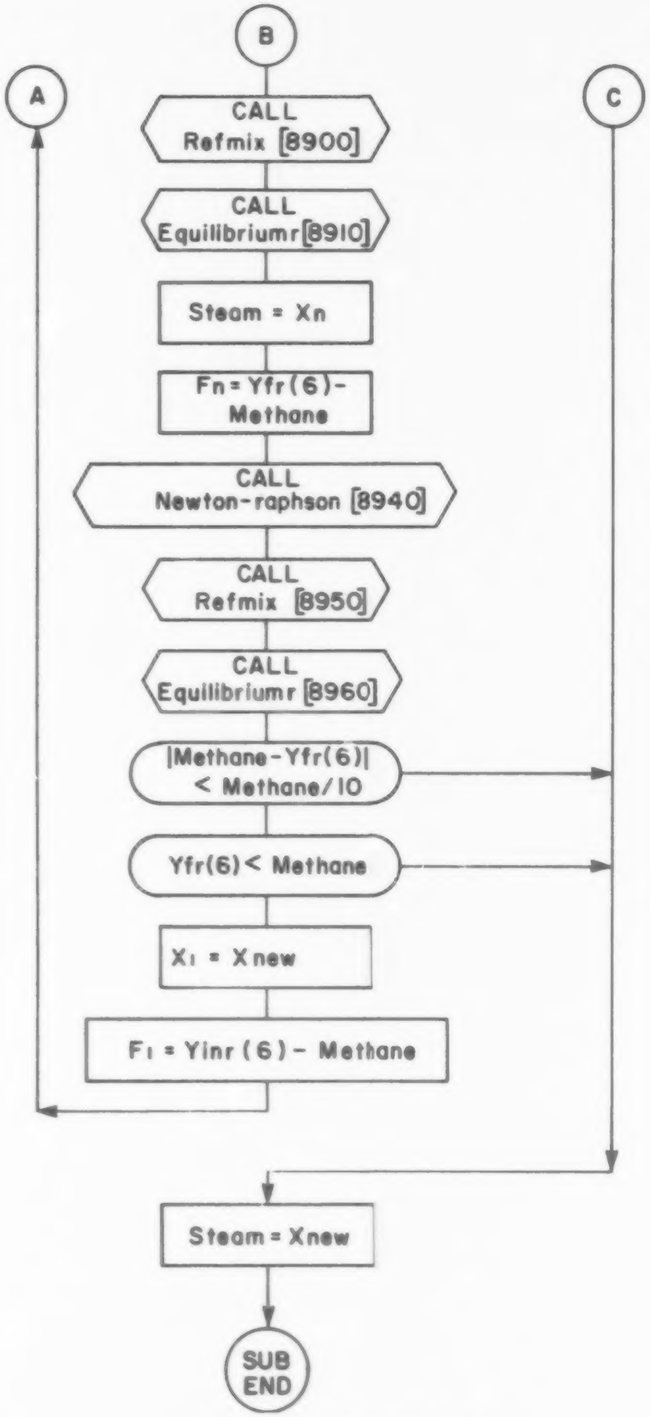

Figure A4. (Concluded)

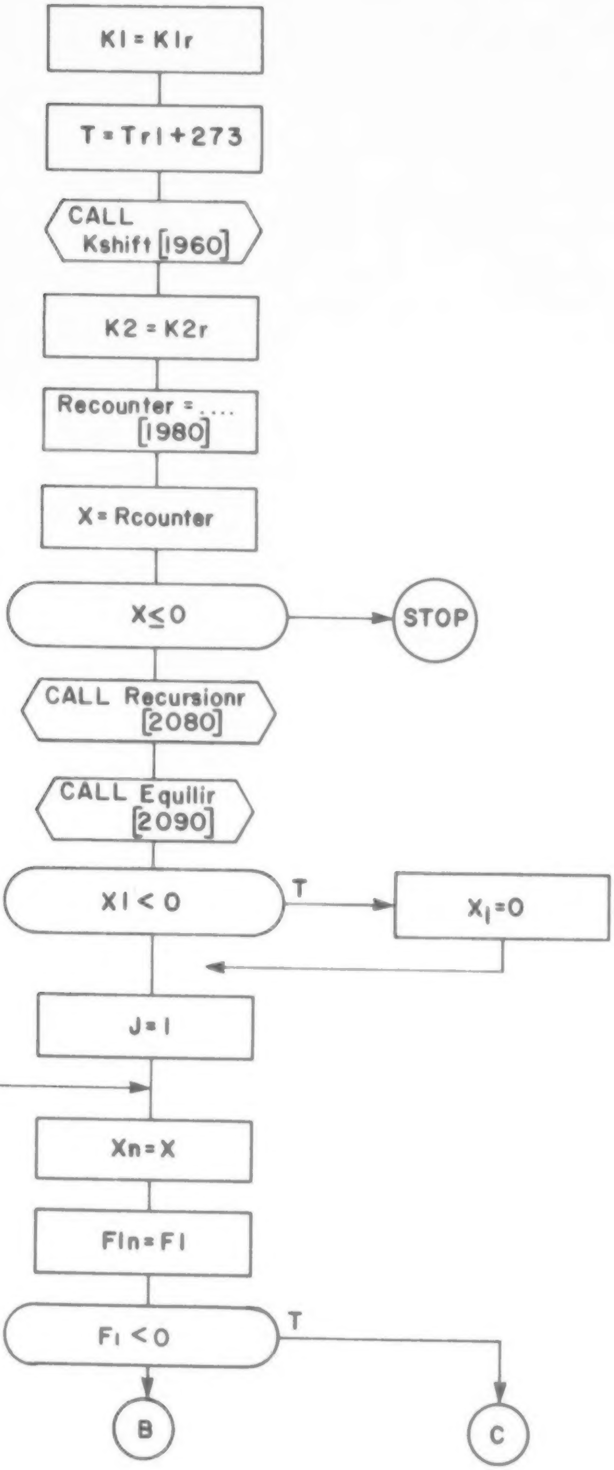

Figure A5. Flow chart for subprogramme "Equilibriumr(Yo(*), Fo)." [], line number in programme listing.

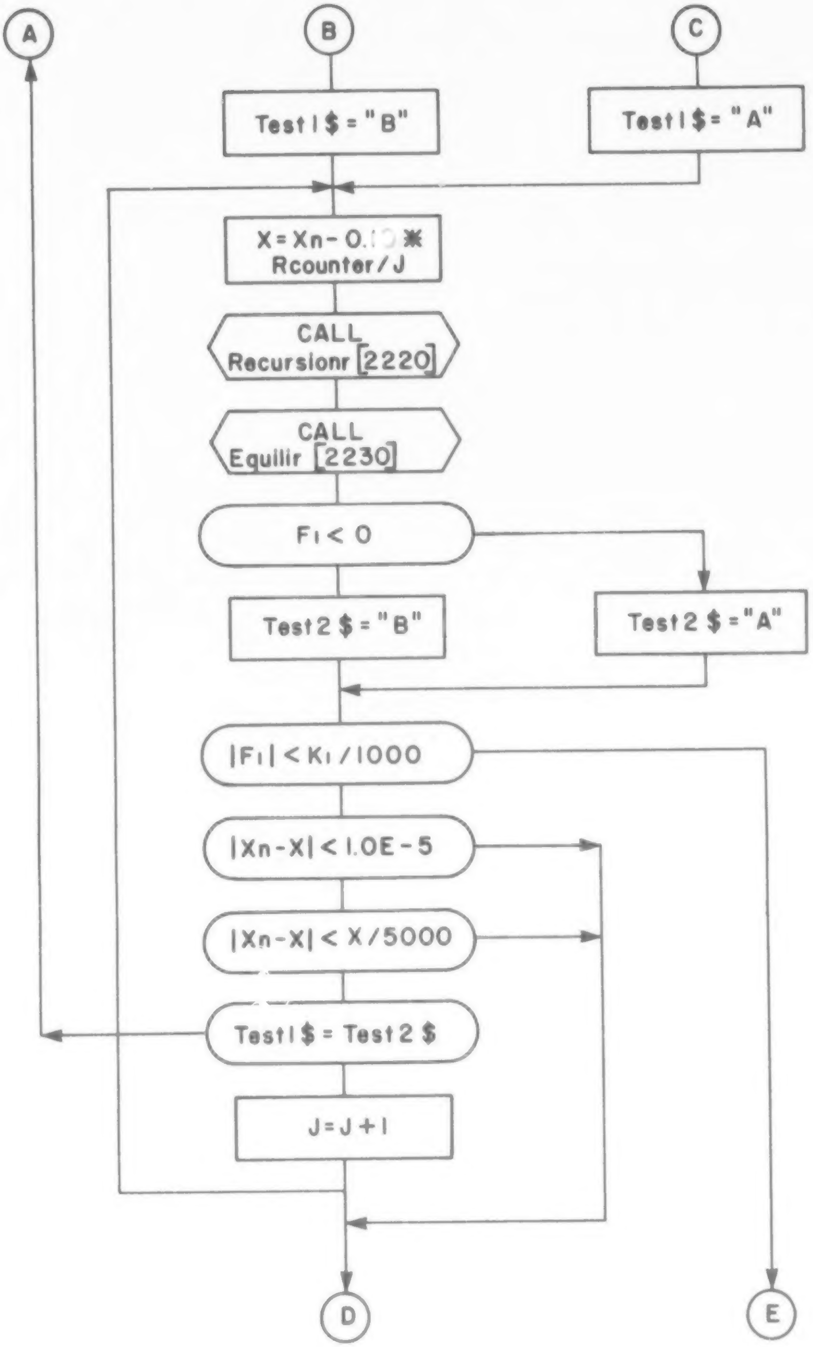

Figure A5. (Continued)

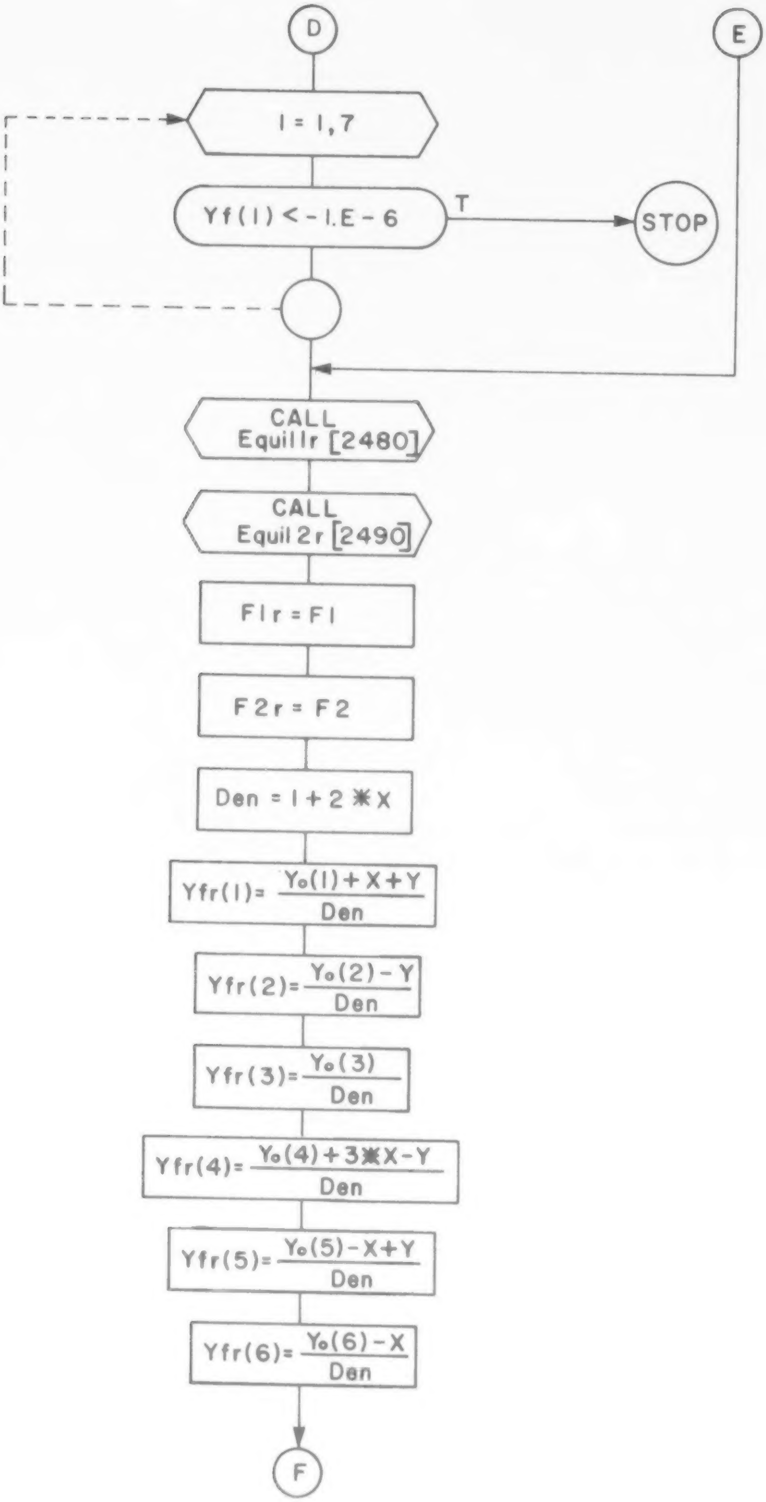
D
E
I = 1,7
Yf(I) < -1.E - 6
T
STOP
CALL Equil1r [2480]
CALL Equil2r [2490]
F1r = F1
F2r = F2
Den = 1 + 2 * X
Yfr(1) = (Yo(1) + X + Y) / Den
Yfr(2) = (Yo(2) - Y) / Den
Yfr(3) = Yo(3) / Den
Yfr(4) = (Yo(4) + 3 * X - Y) / Den
Yfr(5) = (Yo(5) - X + Y) / Den
Yfr(6) = (Yo(6) - X) / Den
F

Figure A5. (Continued)

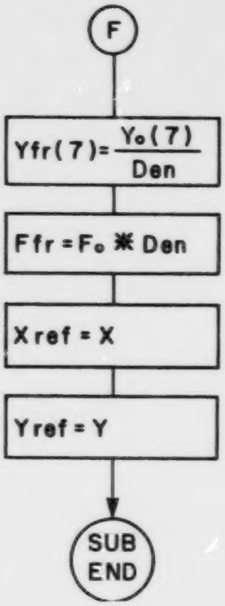

Figure 5. (Concluded).

F1 between it and the input value determined. A step reduction is then made in X and a new F1 is determined. The size of the reduction is variable depending upon the previous value of F1. The procedure is repeated until either of several conditions, shown in the flow chart given in Figure A5, are met. This approach was used since the function describing F1 exhibits hyperbolic characteristics which cause convergence difficulties using standard iterative methods such as Newton-Raphson or false position.

A3.1.2 Recursionr(Yo(*),X,Y,K2)

This subprogramme determines Y for a given X and K2. The flow chart is given in Figure A6.

A description of a number of smaller subprogrammes used in the reformer process module may be obtained from the programme listing.

A3.2 Ht_bal_ref

The function of the subprogramme "Ht_bal_ref" is to determine the quantity of syngas which must be burned to provide heat for the reformer. Due to the recycles involved in the indirect liquefaction process as set up, this subprogramme is executed, in "Process logic," after a mass balance has been obtained for a unit flow of syngas. The first function of the

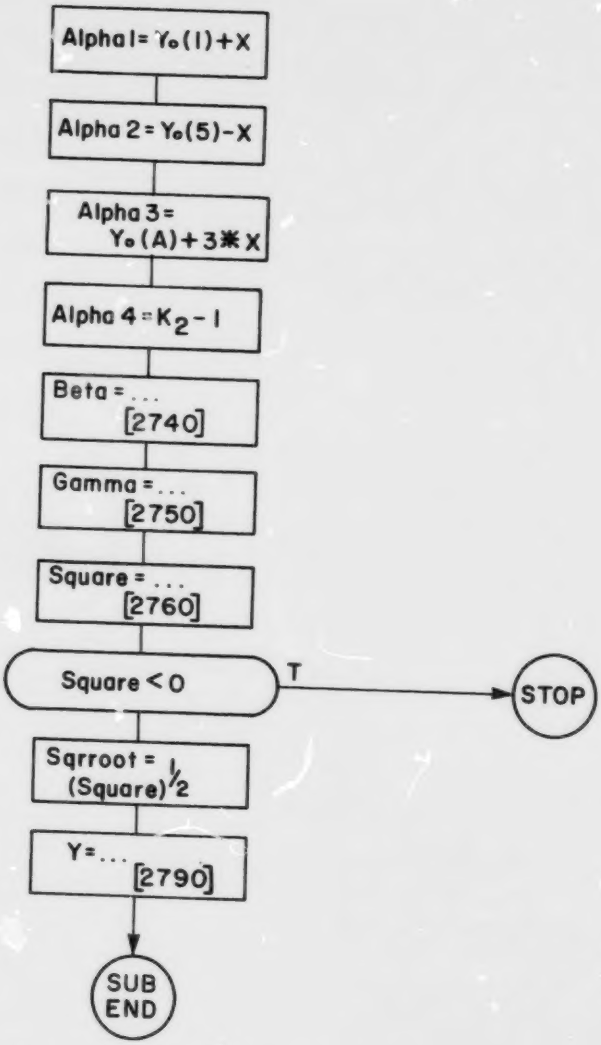

Figure A6. Flow chart for subprogramme "Recursionr(Yo(*),X,Y,K2)."
[ ], line number in programme listing.

programme is to determine the outlet temperatures for the streams leaving the heat exchanger which is shown in Figure A3. When this is completed the heat content for the streams entering and leaving the reformer are determined, as well as the overall heat of reaction. The heat duty of the process unit is then calculated. The available heat from the combustion of syngas with the composition that has been previously specified is determined and knowing the heat duty of the reformer allows the quantitity of syngas to be required for fuel determined. The process flow chart is shown in Figure A7 for this subprogramme.

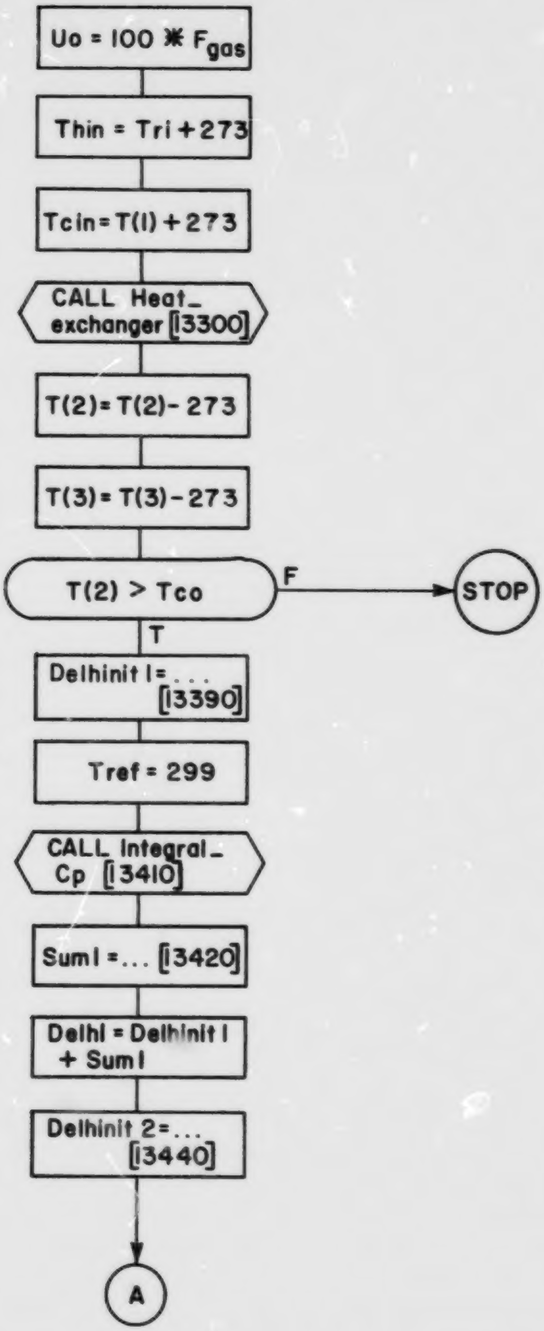

Figure A7. Flow chart for subprogramme "Ht_bal_ref." [], line number in programme listing.

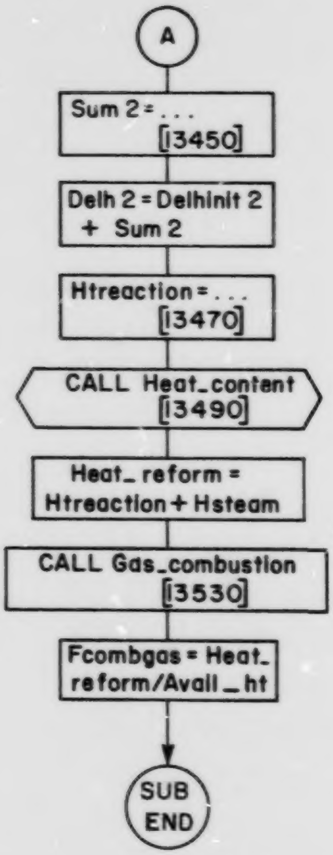

Figure A7. (Concluded).

A3.2.1 Heat exchanger (Yh(*), Fh, Yo(*), Fo, Thin, Tcin, Thout, Tcout, Au)

This subprogramme calculates the outlet temperatures (Thout, Tcout) for a single-pass heat exchanger using the Number-of-Transfer-Units (NTU) method of heat exchanger design. A flow chart is shown in Figure A8.

A3.2.2 Gas combustion(Y(*),F,T1,T2,O2,Avail-ht)

This subprogramme calculates the available heat for the combustion of a gas which has a composition defined by Y(*). A flow chart is shown in Figure A9.

A number of additional small subprogrammes are used in the above in the heat balance calculations. "Integral_cp(T1,T2)" determines the value of the integral of the specific heat with respect to temperature over the interval T1 to T2. "Heat content(Y(*),F,T1,T2,Delh)" determines the heat

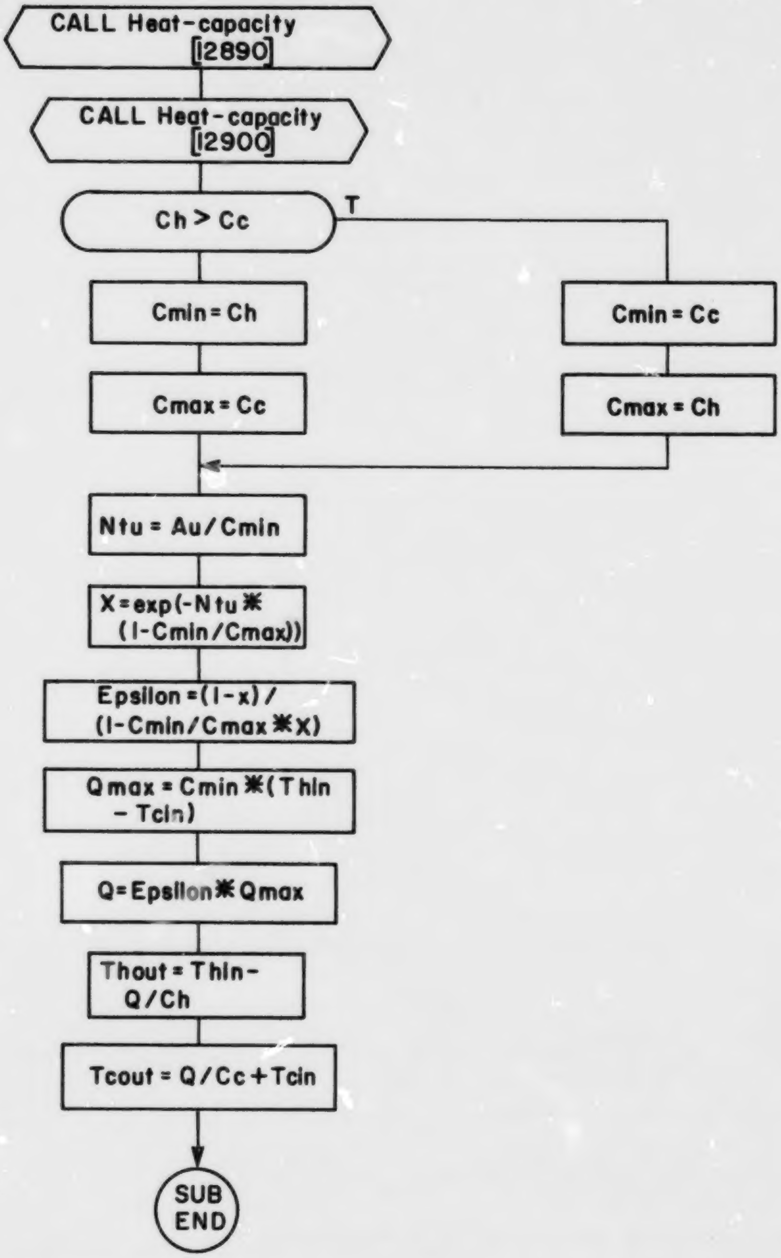
CALL Heat-capacity [12890]
CALL Heat-capacity [12900]
Ch > Cc
T
Cmin = Ch
Cmax = Cc
Cmin = Cc
Cmax = Ch
Ntu = Au/Cmin
X = exp(-Ntu * (1-Cmin/Cmax))
Epsilon = (1-x)/ (1-Cmin/Cmax * X)
Qmax = Cmin * (Thin - Tcin)
Q = Epsilon * Qmax
Thout = Thin- Q/Ch
Tcout = Q/Cc + Tcin
SUB END

Figure A8. Flow chart for subprogramme "Heat_exchanger(Yh(*),Fh,Yo(*),Fo,Thin,Tcin,Thout,Tcout,Au)." [], line number in programme listing.

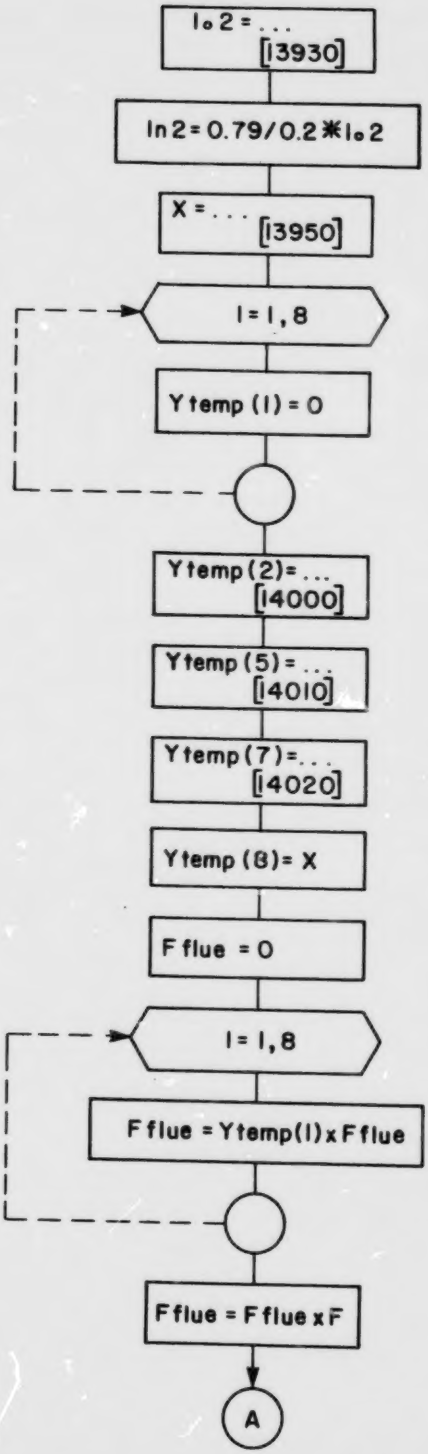

Figure A9. Flow chart for subprogramme as_combustion(Y(*),F,T1,T2,O2,Avail ht)." [], line number in programme listing.

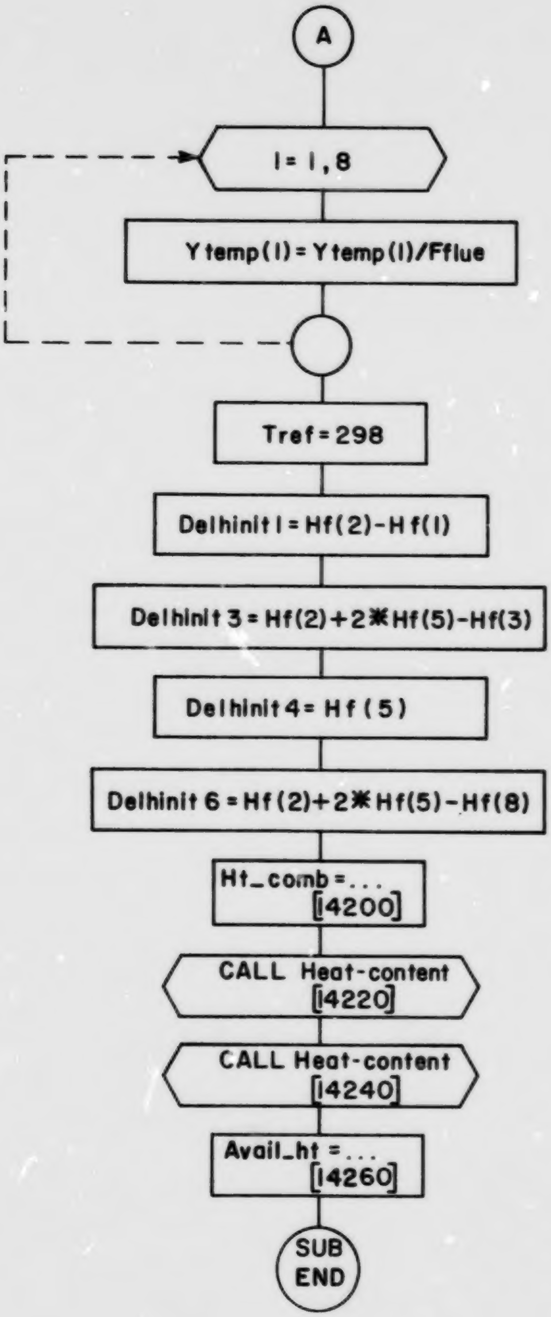

Figure A9. (Concluded)

content of a stream at a temperature of T2 relative to a reference temperature of T1, and "Heat capacity (Y(*), F, T, Cp)" calculates the heat capacity of a stream having a composition defined by Y(*) and at a temperature of T.

A4.0 CO SHIFT AND ACID GAS REMOVAL

A4.1 CO shift and Acid rem(Yinacid (*), Finacid, Yfacid(*), Ffacid)

The process flow for the CO shift and the Acid Gas Removal process units is shown in Figure A10 and the nomeclature used is given in Table A2. The objective of these two units is to produce a syngas having a balance ratio of 2.1 and specified CO_2 and H_2O concentrations. The flow chart for the CO_shift subprogramme is shown in Figure A11 and its function is to check on whether or not this process unit is required in the circuit. This is done by by-passing the unit and determing the resultant balance ratio after the acid gas removal unit. If the balance ratio is greater than 2.1 then the calculations for these units are completed and the subprogramme ends. If the balance ratio is less than 2.1 then the entire syngas flow is processed in the CO shift unit. If the balance ratio after the acid gas

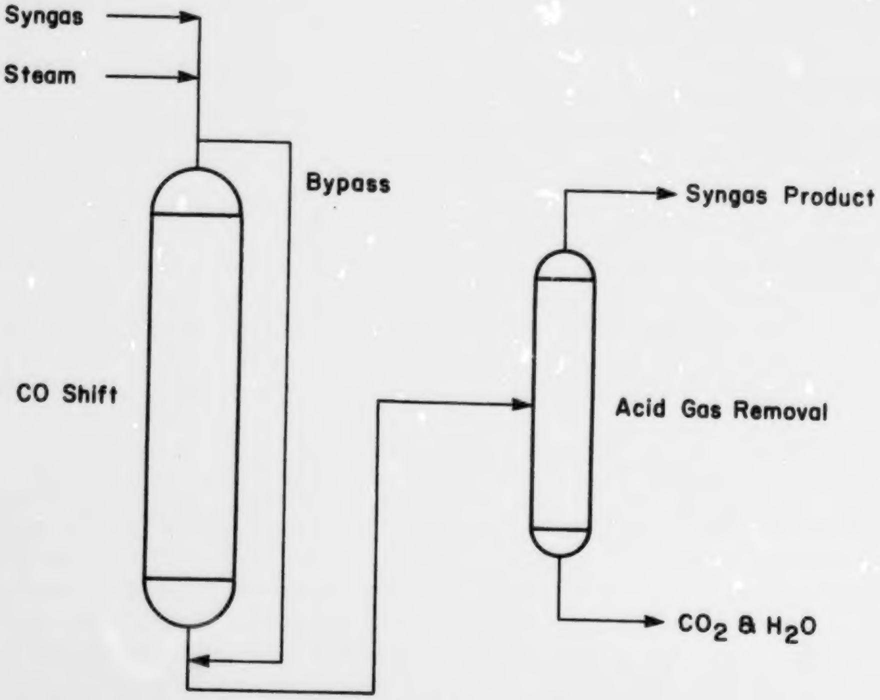

Figure A10. Schematic of CO shift and acid gas removal units.

Table A.2. Nomenclature for the Subprogrammes "Co-shift" and "Acid-rem"

Species :
  CO : 1
  CO_2 : 2
  CH_3OH : 3
  H_2 : 4
  H_2O : 5
  CH_4 : 6
  N_2 : 7
  O_2 : 8
Fbyco : molar flow rate of stream bypassing CO Shift unit
Fcosteam : molar flow rate of steam fed to CO Shift unit
Ffacid : molar flow rate of product stream from Acid Removal unit
Ffco : molar flow rate of product stream from CO Shift unit
Finacid : molar flow rate of feed stream to Acid Removal unit
Finco : molar flow rate of feed stream to CO Shift unit
Foutco : molar flow rate of reactor outlet stream in CO Shift unit
Pco : reactor pressure in the CO Shift unit, atm.
Tco : reactor temperature in the CO Shift unit, °C.
Yfacid(i) : molar concentration of component "i" in product stream from Acid Removal unit
Yfco(i) : molar concentration of component "i" in product stream from the CO Shift unit
Yfco2 : molar concentration of CO_2 in product stream from the Acid Removal unit
Yfh2o : molar concentration of H_2O in product stream from the Acid Removal unit
Yinacid(i): molar concentration of component "i" in feed stream to the Acid Removal unit (same as Yfco(i))
Yinco(i) : molar concentration of component "i" in feed stream to the CO Shift unit
Youtco(i) : molar concentration of component "i" in reactor product in Acid Removal unit

unit is greater than 2.1 then a by-pass flow around the CO shift unit is determined using a Newton-Raphson iterative procedure. The target value for the balance ratio is 2.1 ± 0.5%. If the balance ratio is less than 2.1 when the entire process stream is processed by the unit then steam is added to the feed so that the shift reaction produces the specified balance ratio. A Newton-Raphson iterative procedure is again employed to determine the quantity of steam required. The Acid_rem subprogramme determines the composition and flow rate of the syngas for given feed conditions and given

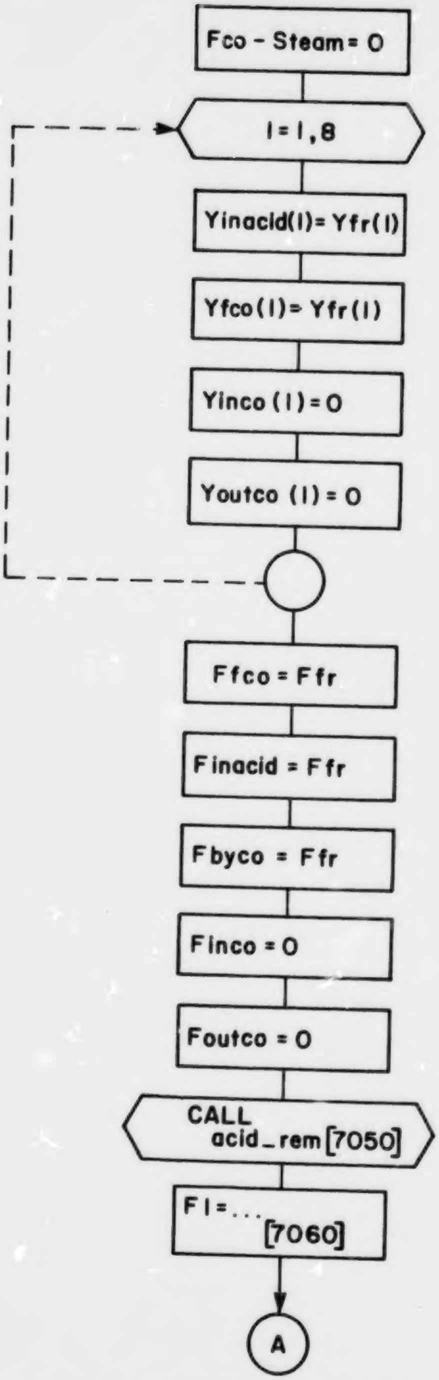

Figure A11. Flow chart for subprogramme "CO_shift." [], line number in programme listing.

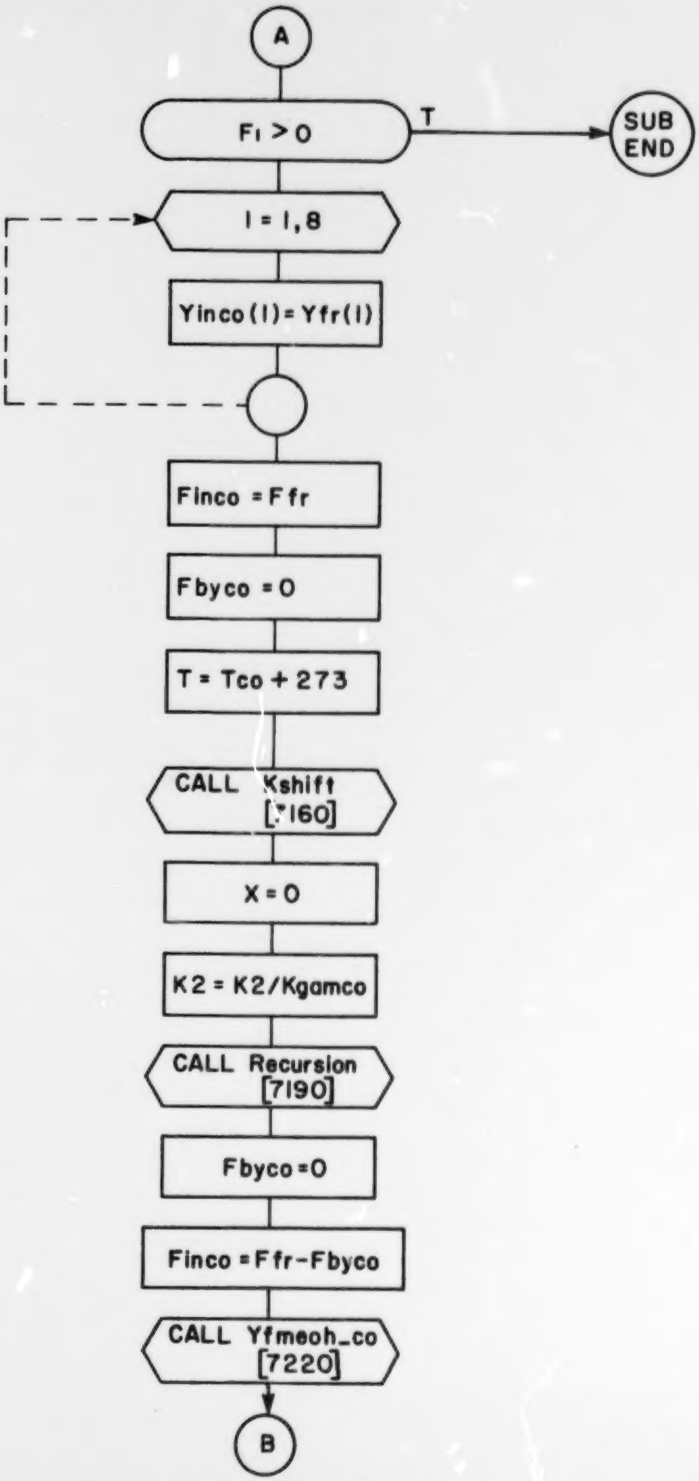

Figure A11. (Continued)

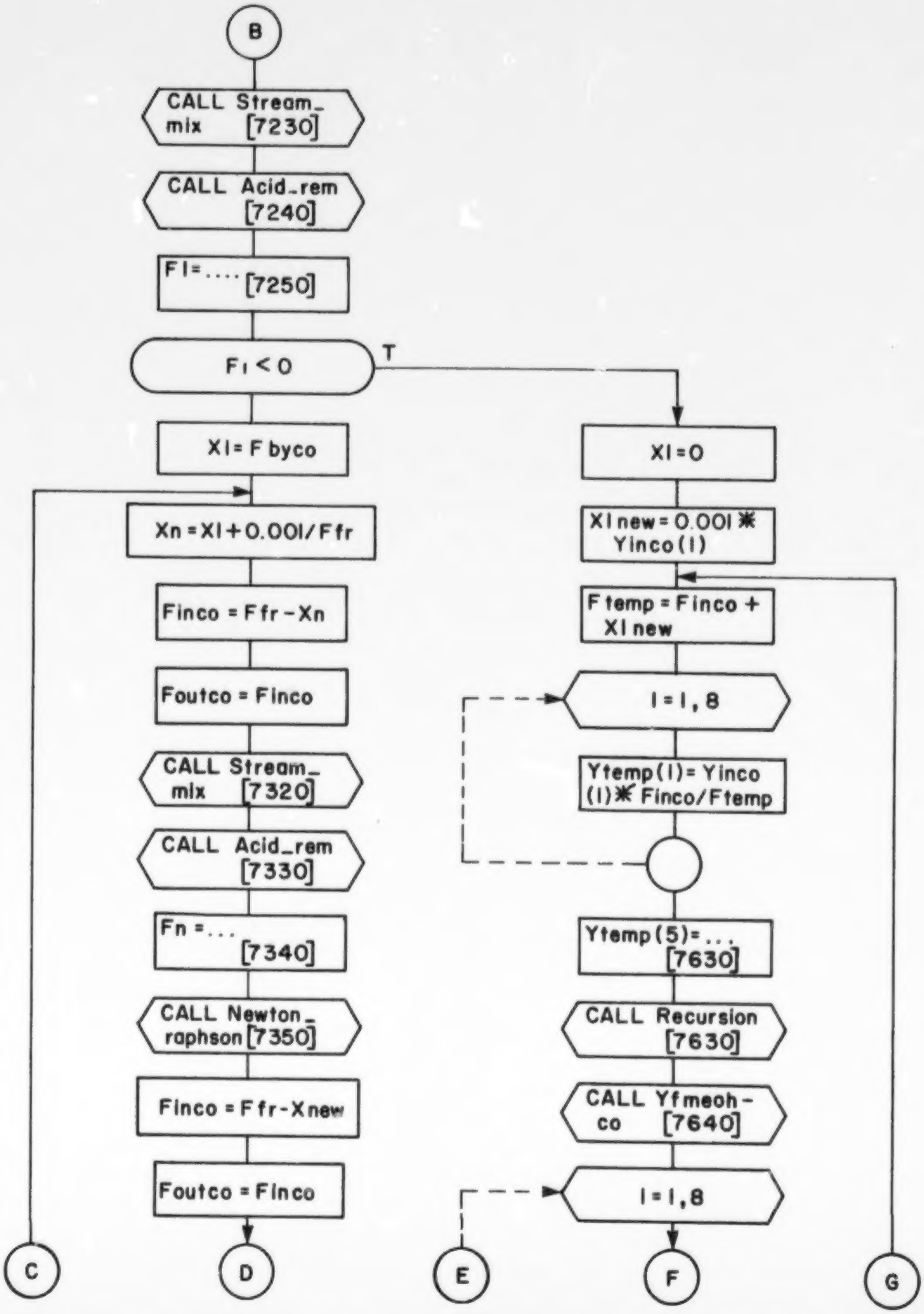

Figure A11. (Continued)

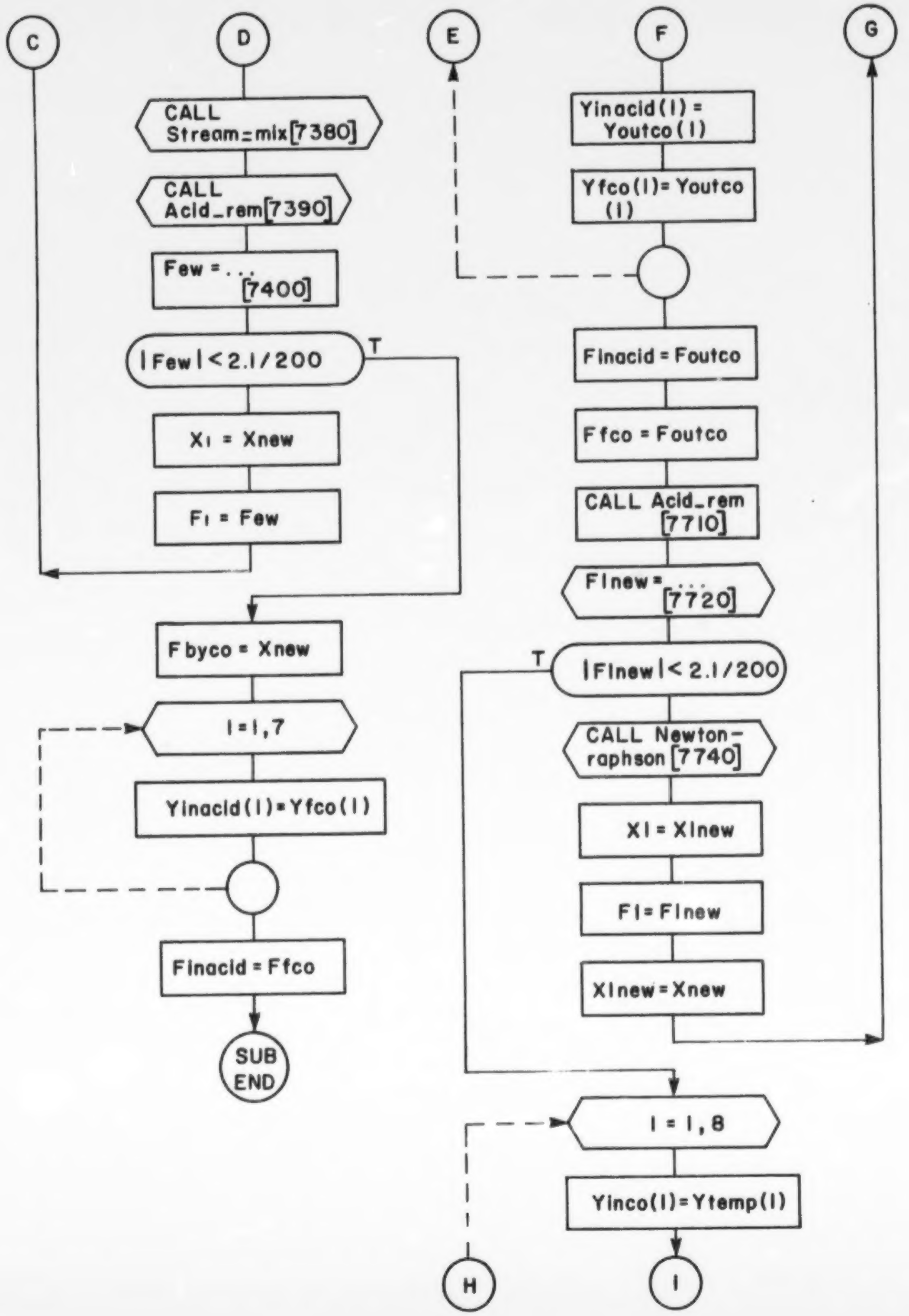

Figure A11. (Continued)

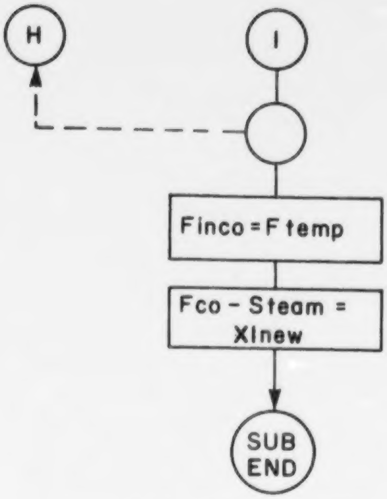

Figure A11. (Concluded)

concentrations of CO_2 and H_2O in the product flow. In the current programme the CO_2 concentration is set at 4% and all of the H_2O is removed. The flow chart for the Acid_rem subprogramme is shown in Figure A12.

A5.0 METHANOL

A5.1 Methanol(Yinput(*),Finput)

A schematic diagram of the process flow for the methanol process unit is shown in Figure A13. This programme determines the production rate of methanol, as well as the composition and flow of the purge stream from the unit. The flow rate of the internal recycle stream which returns a portion of the syngas from the purification section (distillation) may be specified, relative to the feed rate to the unit, or it may be calculated. In the latter case the concentration of methane in the recycle stream must be specified. An iterative procedure is used in the programme until the purge rate of methane converge to within 1% of the feed rate to the unit for the case in which the recycle rate is specified. For the case in which the methane concentration is specified the iteration is terminated when the concentration of methane in the recycle stream converges to within 1% of the target value. A process flow chart for the subprogramme is shown in Figure A14 and the nomenclature used is given in Table A3. Major subprogrammes called by "Methanol" are discussed below.

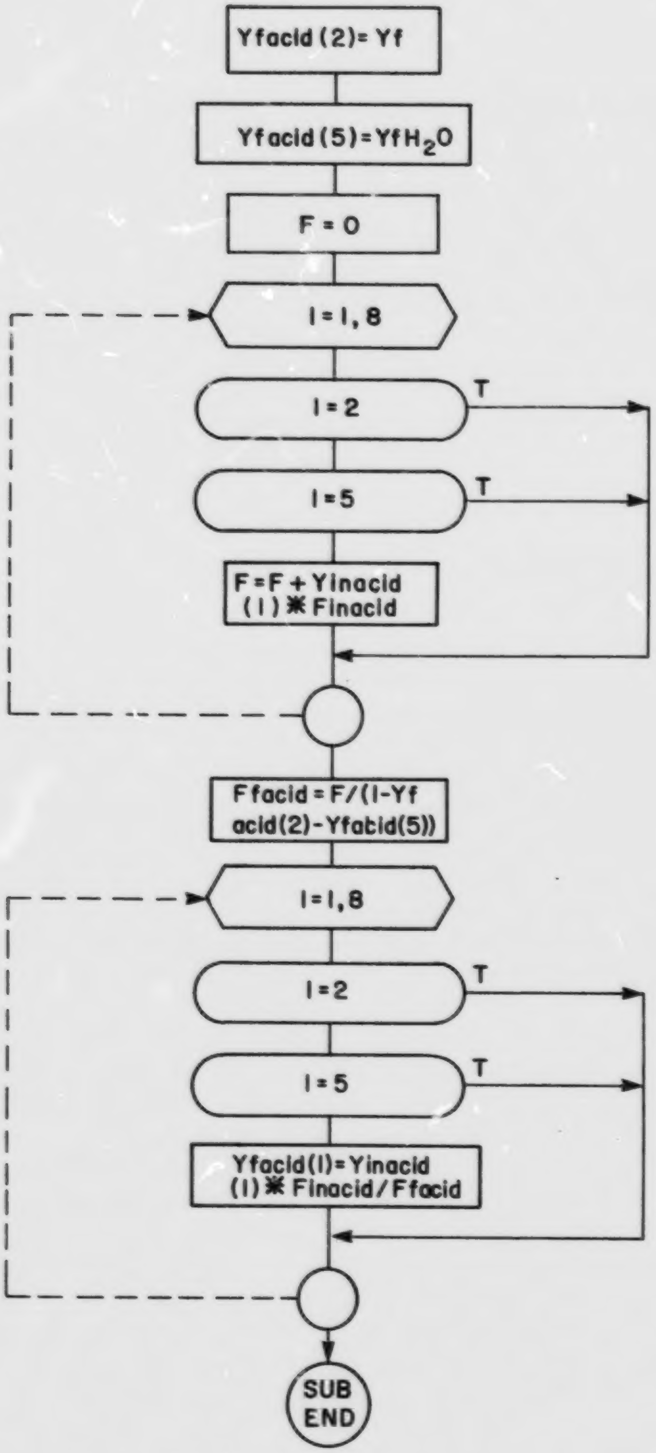

Figure A12. Flow chart for subprogramme "Acid_rem(Yinacid(*),Finacid,Yfacid(*),Ffacid."

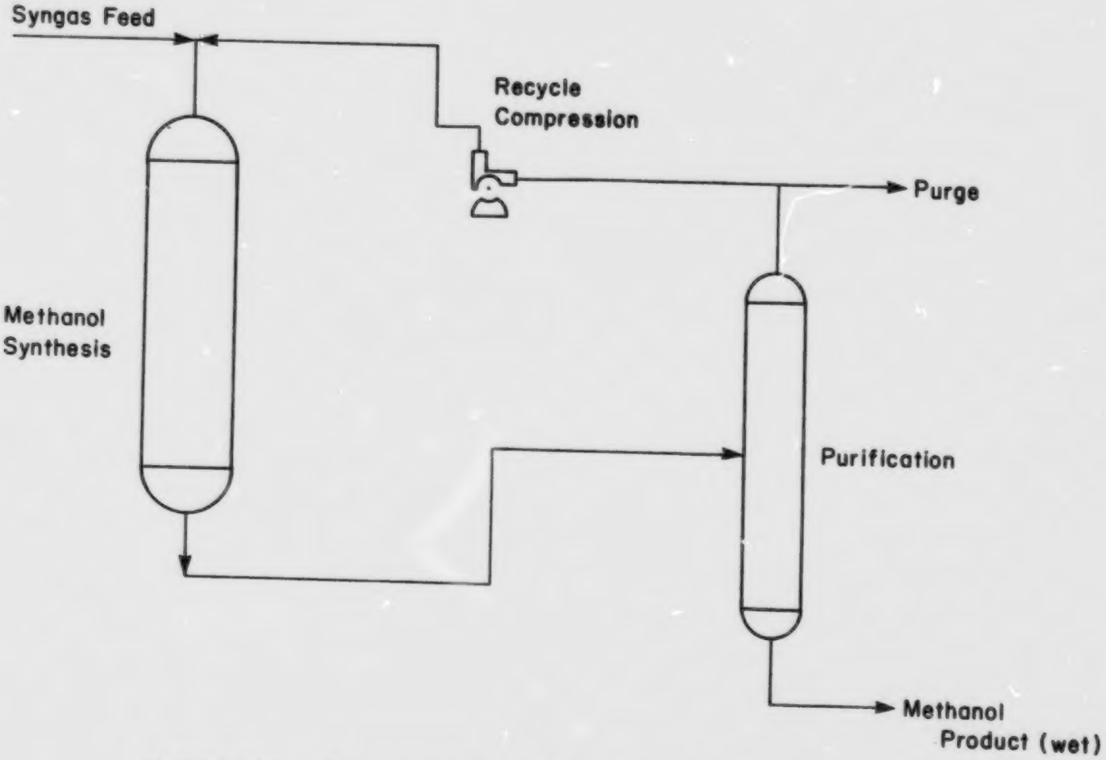

Figure A13. Process schematic of methanol synthesis unit.

A5.1.1 Equilibrium(Yin(*),Fin,Yf(*) ,Fout)

This subprogramme, analogous to the subprogramme "Equilibriumr" given in Section A3.1.1, determines the equilibrium composition for a given feed composition, temperature, and pressure. The two reactions considered in the calculations are the reaction of CO with H_2 to form CH_3OH and the inverse water gas shift reaction, as illustrated below.

[A3] $CO + 2H_2 = CH_3OH$

[A4] $CO_2 + H_2 = CO + H_2O$

In the programme X is the production of CH_3OH in reaction [A3] and Y is the conversion of CO_2 in reaction [A4]. The equilibrium constants are calculated given the temperature, pressure, and equilibrium coefficient formed from the activity coefficients. The procedure is identical to that followed in "Equilibrium." A process flow chart for this subprogramme is shown in Figure A15.

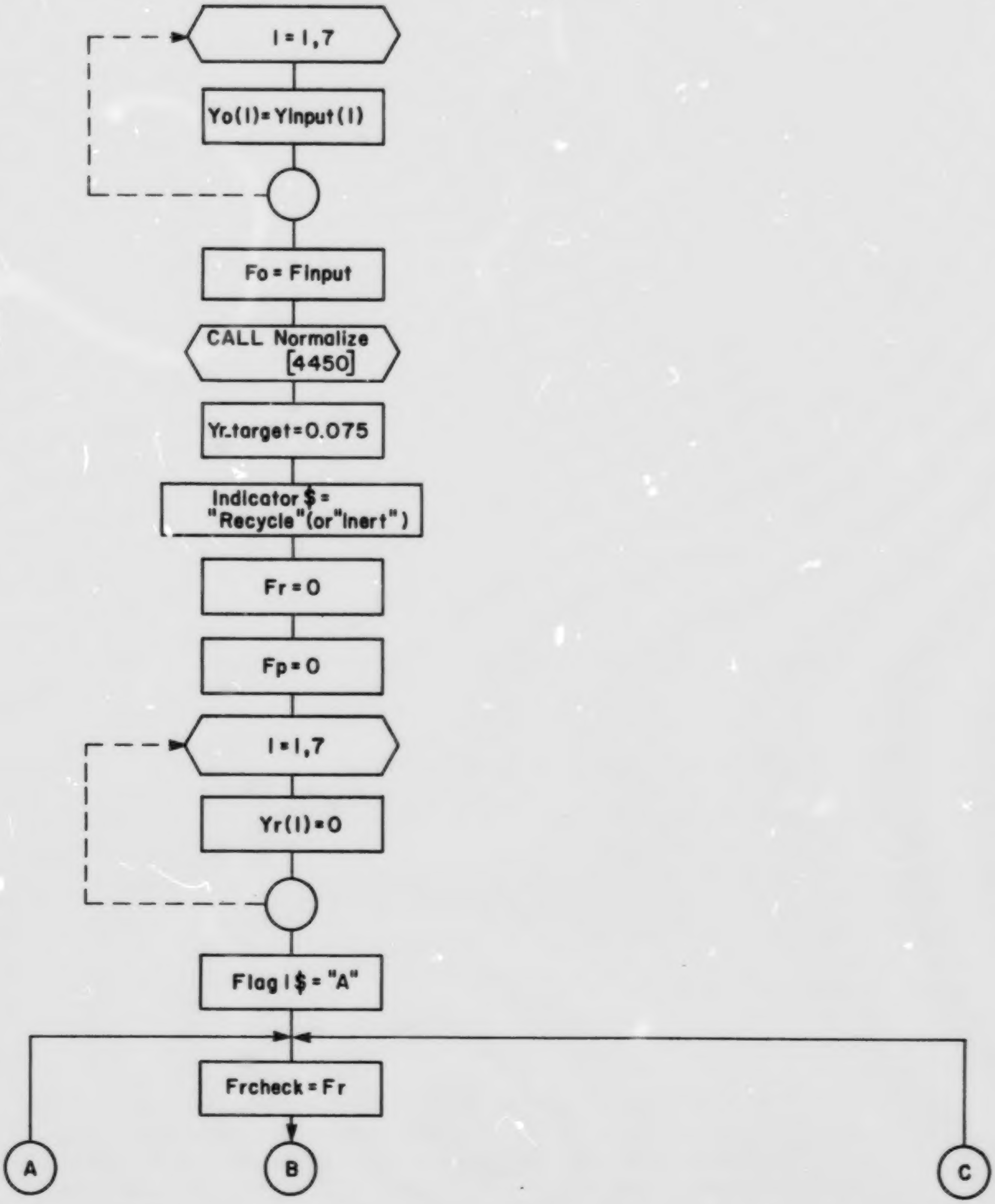

Figure A14. Flow chart for subprogramme "Methanol(Yinput(*),Finput)." [], line number in programme listing.

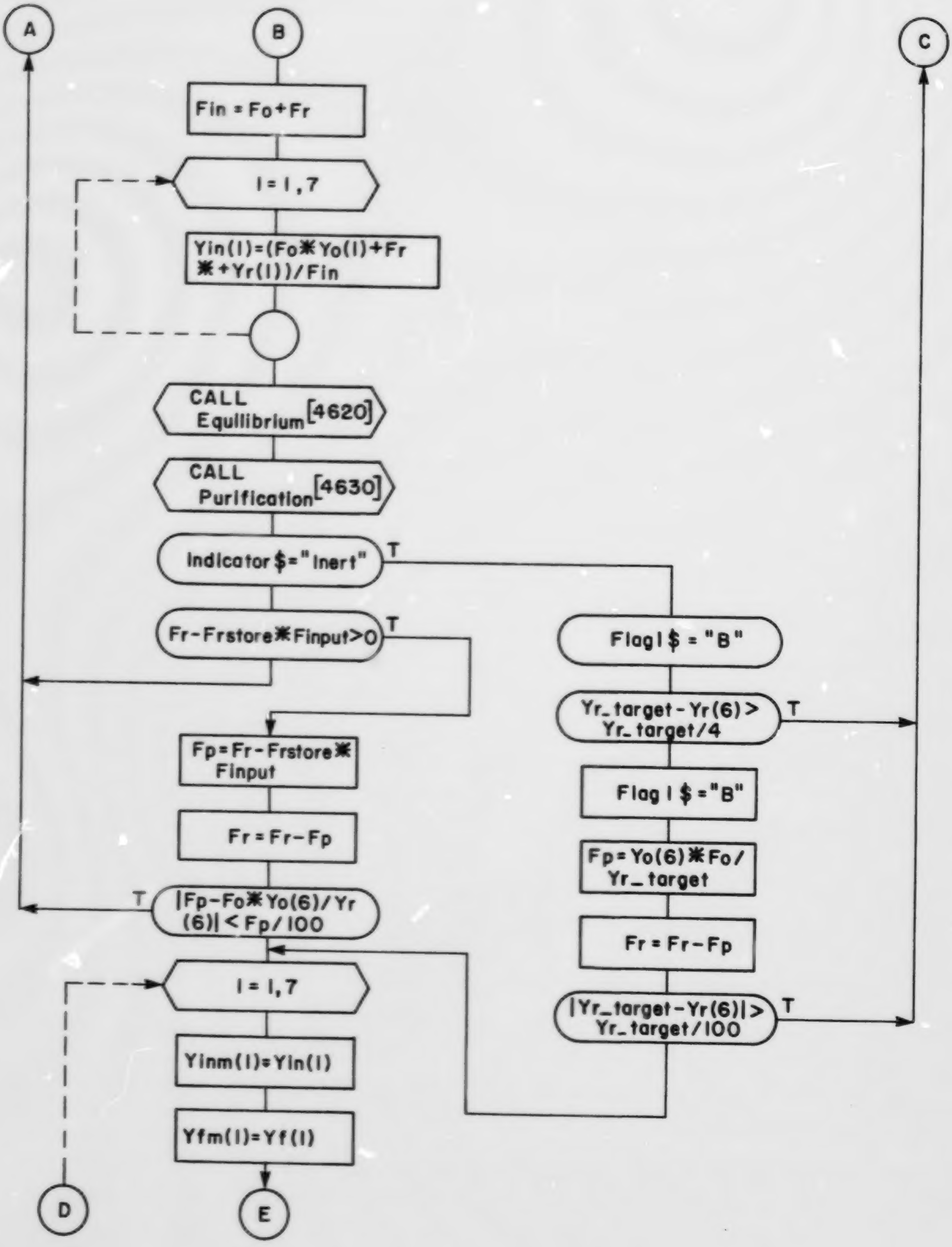

Figure A14. (Continued).

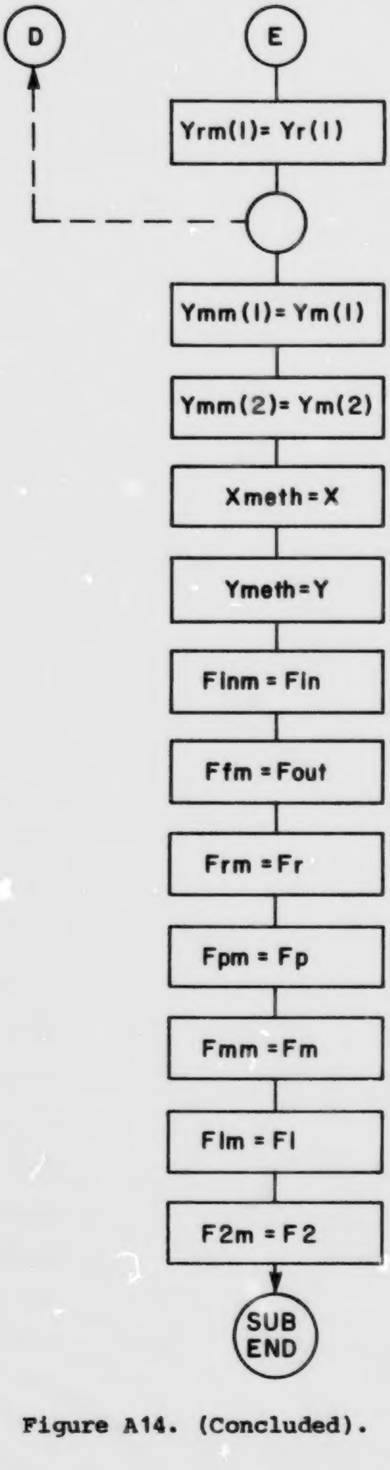

Figure A14. (Concluded).

Table A3. Nomenclature for the Subprogramme "Methanol"

Species :

CO : 1

CO_2 : 2

CH_3OH : 3

H_2 : 4

H_2O : 5

CH_4 : 6

N_2 : 7

O_2 : 8

for Ymm(i):

CH_3OH : 1

H_2O : 2

Ffm : molar flow rate of methanol reactor product stream

Finm : molar flow rate of methanol reactor feed stream

Fmm : molar flow rate of methanol product stream from unit

Fo : molar flow rate of synthesis gas to unit

Fpm : molar flow rate of purge stream from unit

Frm : molar flow rate of recycle stream

Frstore : molar ratio of the recycle to feed streams (=Frm/Fo)

Yfm : molar concentration of component "i" in reactor product stream

Yinm(i) : molar concentration of component "i" in reactor feed stream

Ymm(i) : molar concentration of component "i" in methanol product stream leaving unit

Yo(i) : molar concentration of component "i" in feed to unit

Yrm(i) : molar concentration of component "i" in internal recycle stream

A5.1.2 Recursion(Yo(*),X,Y,K)

This subprogramme determines Y for a given X and K. The flow chart is given in Figure A16.

A description of a number of smaller subprogrammes used in the methanol process unit may be obtained from the programme listing.

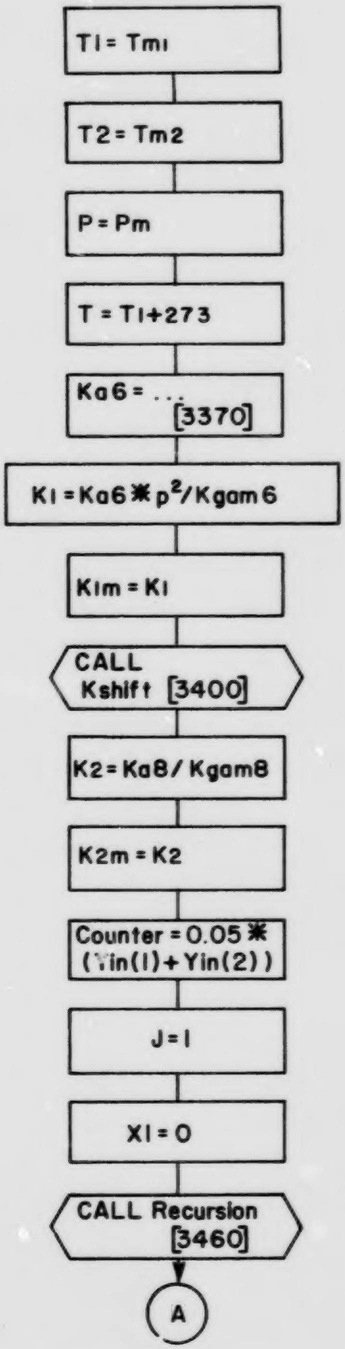

Figure A15. Flow chart for subprogramme "Equilibrium(Yin(*),Fin,Yf(*),Fout)." [], line number in programme listing.

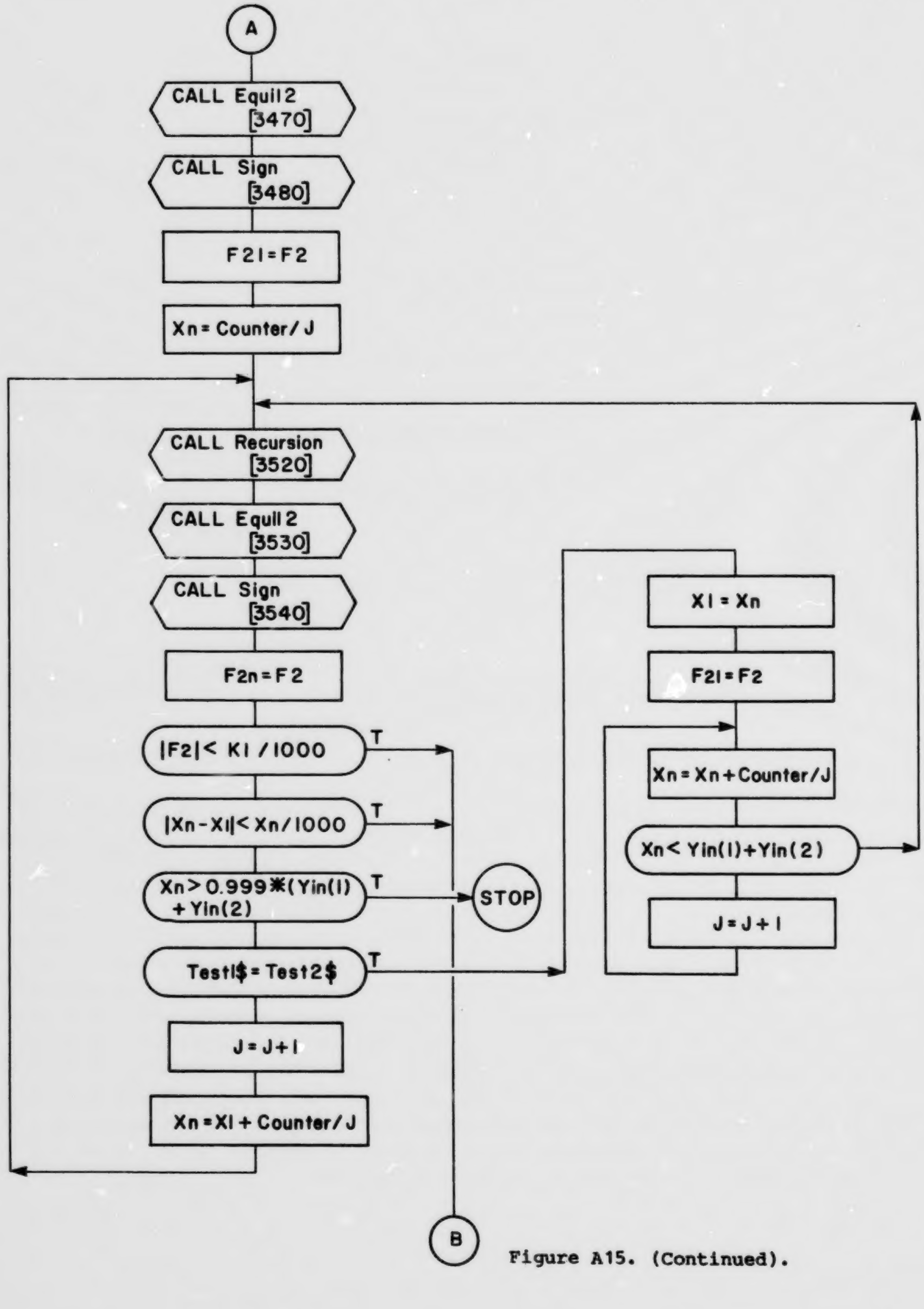

Figure A15. (Continued).

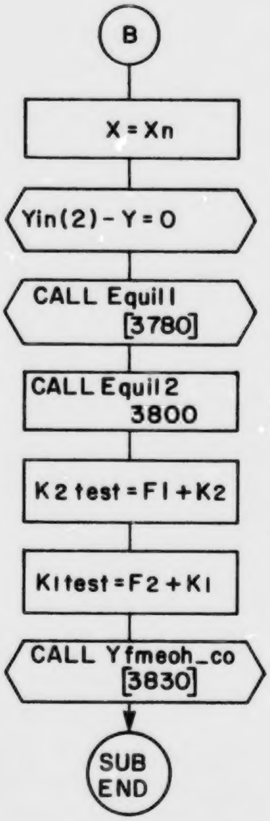

Figure A15. (Concluded).

A6.0 GASIFIER

A6.1 Gasifier(Y(*),F,Char-yield,Tsteam,Tgas,Fwood, Fsteam,Fchar,Fo2,Fhso,-Fcond,Fgasifier,Ygasifier(*),Ext-ht supply,Type$)

A heat and mass balance on the gasifier, shown schematically in Figure A17, is produced using the subprogramme "Gasifier." The flow rates of wood, steam, and char are determined based on the specified syngas composition and the wood characteristics. If a negative steam feed rate is calculated then it is assumed that condensation of water has occurred in the syngas stream prior to the point of analysis. The steam feed rate is then set at zero, and the composition of the syngas produced by the gasifier is determined. A heat balance is used to determine the quantity of heat which is either generated by the gasifier or removed by it. A flow chart for this subprogramme is shown in Figure A18.

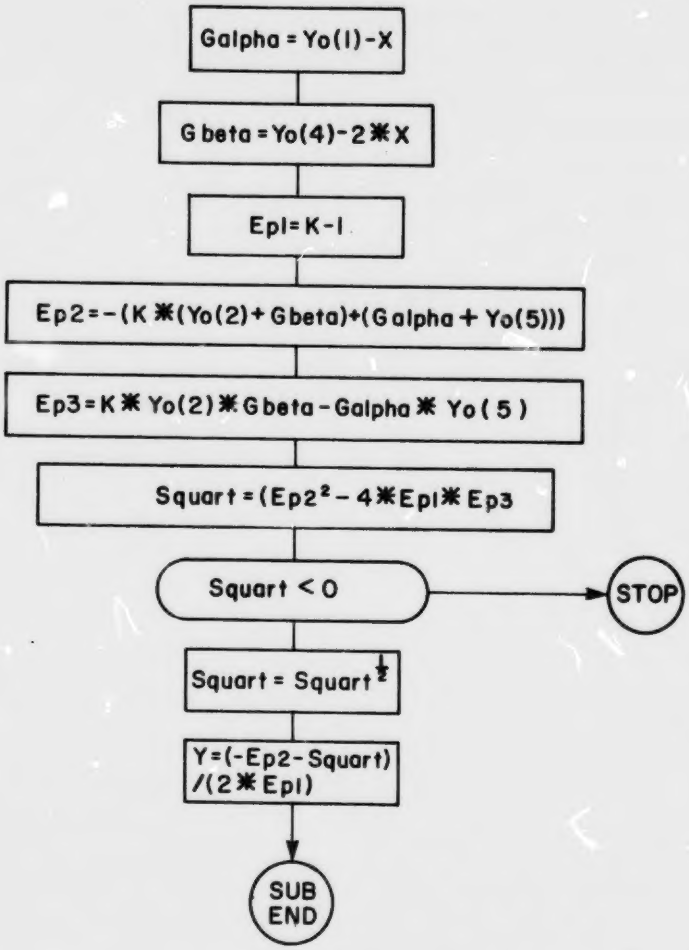

Figure A16. Flow chart for subprogramme "Recursion(Yo(*),X,Y,K)."

A number of small subprogrammes are used in this programme. Gasifier water(Y(*), F,Fsteam,Fcond) determines the quantity of water which has condensed from the syngas, if the mass balance produced a negative steam feed rate, and determines the composition of syngas produced by the gasifier. Bcl_combustor (Fchar,Tgas,0.05,Ext-ht-supply) is used only if the BCL gasifier is used in the process and hence steam gasification occurs. This subprogramme determines the quantity of char which must be burned in order to provide heat for the gasification reactions. Char produced by the gasifier is used as the fuel. The subprogrammes "Integral cp" and "Heat content" are also used and have been described previously under Section A3.2 "Ht_bal ref".

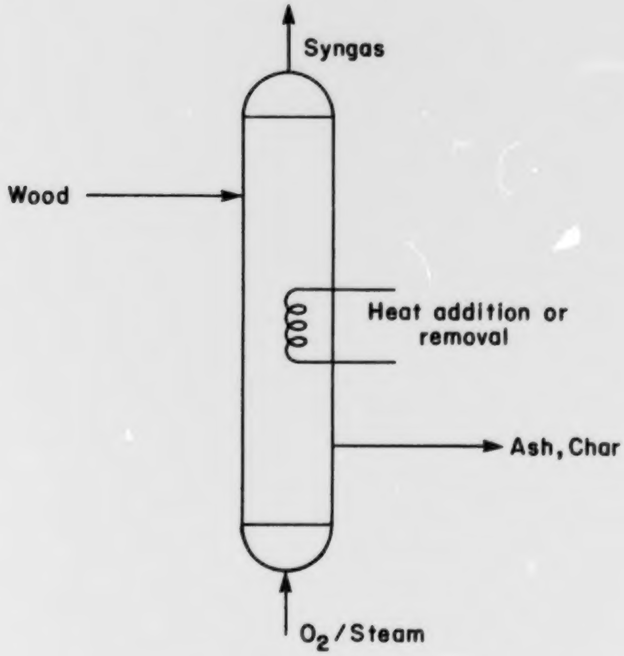

Figure A17. Schematic of gasifier.

A7.0 OXYGEN

A7.1 Oxygen(F,Power)

The power requirements for the cryogenic production of oxygen is determined in this subprogramme. A linear relationship is assumed between power requirements and oxygen flow.

A8.0 DRYER

A8.1 Dryer

This subprogramme determines the quantity of wet wood which must be fed to the dryer based on the wood feed requirements of the gasifier and the characteristics of the wet wood. A portion of the dry wood produced by the dryer is burned in order to provide heat for the drying process. A schematic diagram of the dryer is shown in Figure A19.

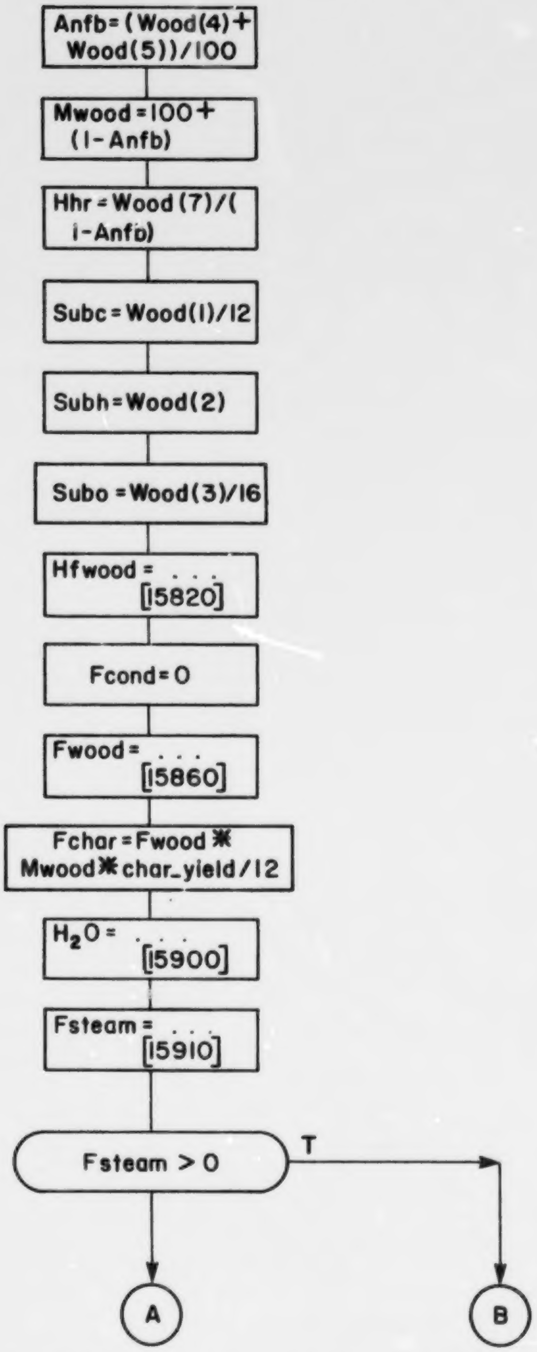

Figure A18. Flow chart for subprogramme "Gasifier(Y(*),F,Char_yield,Tsteam,Tgas,Fwood,Fsteam,Fchar,FO2,FH2O,Fcond,Fgasifier,Ygasifier(*),Ext_ht_supply,Type$)." [], line number in programme listing.

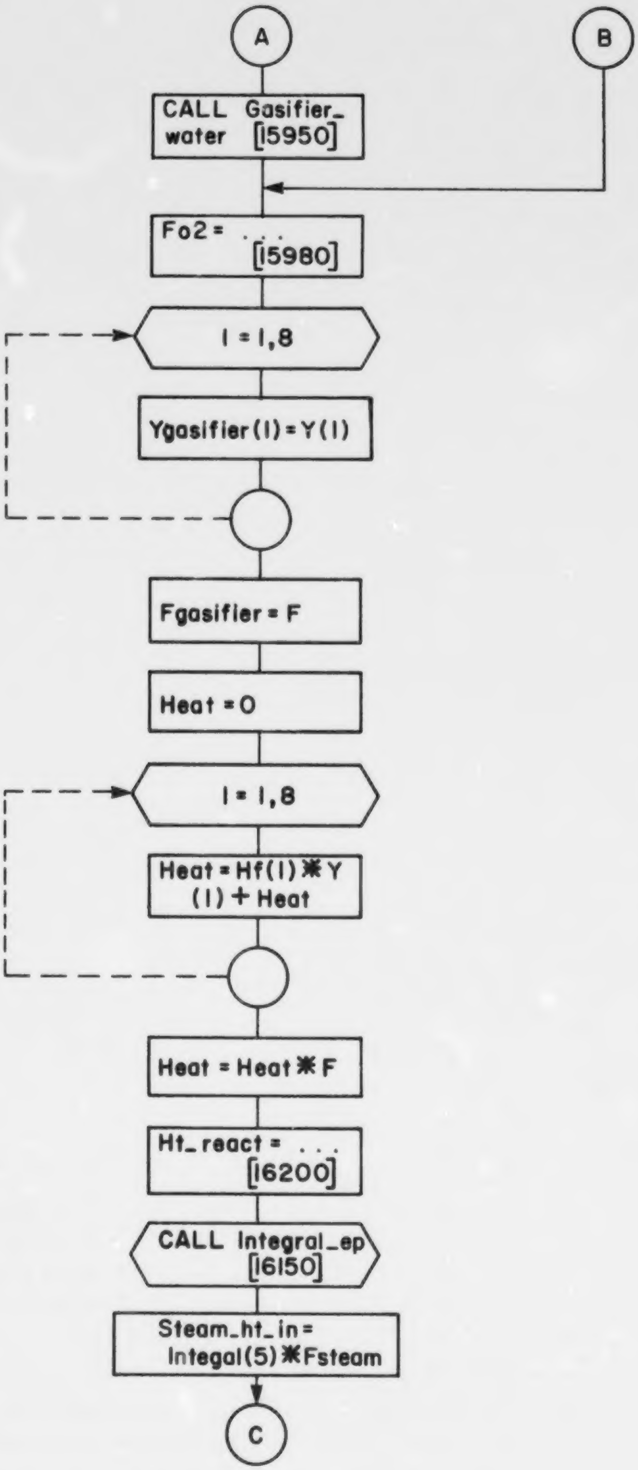

Figure A18. (Continued).

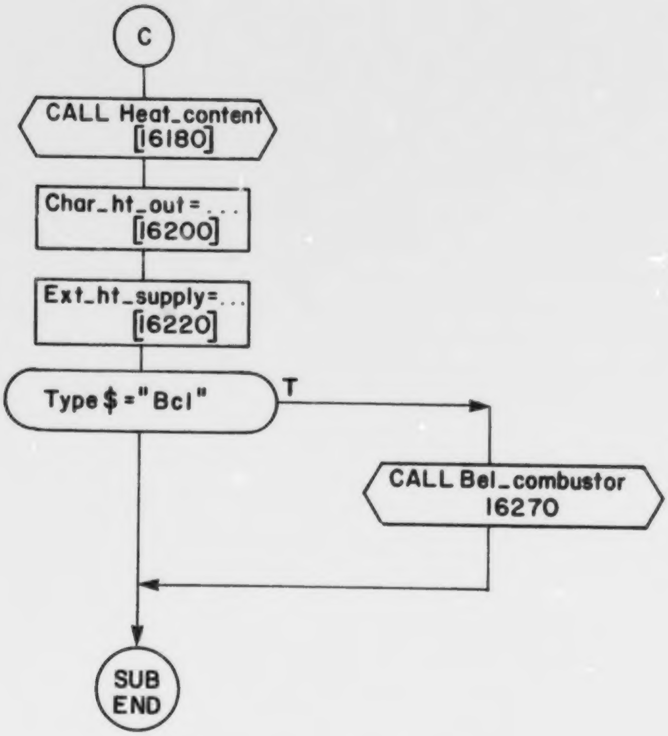

Figure A18. (Concluded).

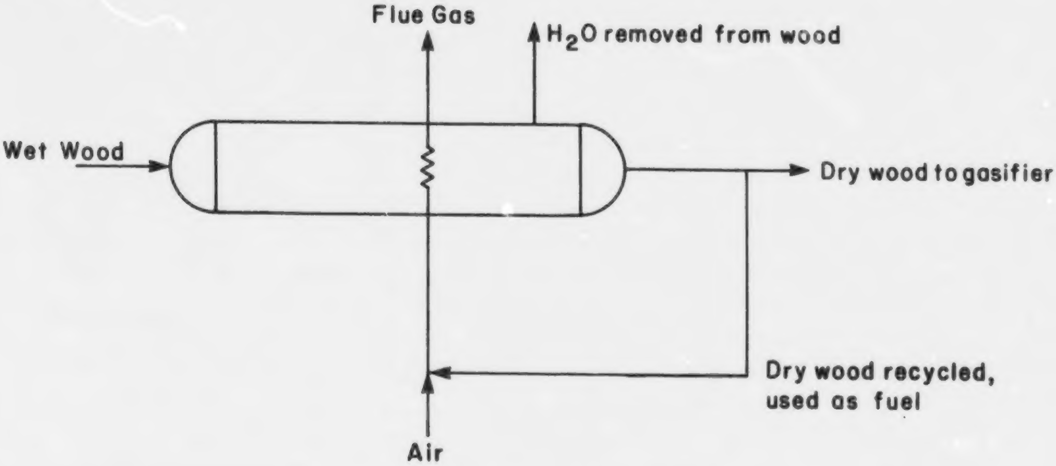

Figure A19. Schematic of dryer.

A9.0 COMPRESSOR

A9.1 Compressor (Y(*),F,T1,T2,P1,P2,Hcomp)

This subprogramme is used to determine the shaft power required for the compression of either the main syngas stream or the recycle stream in the methanol unit assuming polytropic compression and using the "N" method of calculation. A polytropic efficiency of 0.76 is assumed (Elliot compressor frame 29M) and the efficiency due to bearing and seal losses is 0.96. An iterative procedure is used since an average compressibility factor is required in the calculation. Convergence is assumed to be acceptable when there is less than a 1% difference in the average compressibility factor between iterations. A flow chart for this subprogramme is shown in Figure A20.

The compressibility factor required by the "Compressor" subprogramme is determined using the subprogramme "Eqn state(Y(*),T,P,Z)". The Redlick Kwong equation of state is used in the calculation.

A10.0 BOILER

A10.1 Boiler(Fboiler-wood, Mw, Mcwood, Fc, Mc-char, Subc, Subh, Subo, Tls, Ths, = Comp-power, Turbine eff, Boiler-stack o2,Hfwood, Avail-ht, Fst, Ext-ht,Fsteam)

It is assumed that the power for compression in the methanol process unit and the main syngas flow stream and for the gasifier external heat supply is produced using a boiler with a non-condensing steam turbine as shown in Figure A21. The external heat supply to the gasifier is also considered to be provided by electrical resistance heating, therefore a generator efficiency of 0.95 is also assumed (note: overall efficiency would also include that for boiler and turbine). Char produced by the gasifier is used to feed the boiler. If the char production rate is insufficient to meet power requirements then wet wood is also mixed with the char. In this case a Newton-Raphson iterative procedure is used to calculate the wood feed rate and convergence is assumed complete when there is less than 0.5% difference between the generated power and the required power. A flow chart for this subprogramme is shown in Figure A22.

Several small subprogrammes are required by the "Boiler" subprogramme. The subprogramme "Turbine (Tlower steam,Thigher steam,Comp-power,Turbine eff,=Heat duty,Fsteam boiler)" determines the heat duty and steam

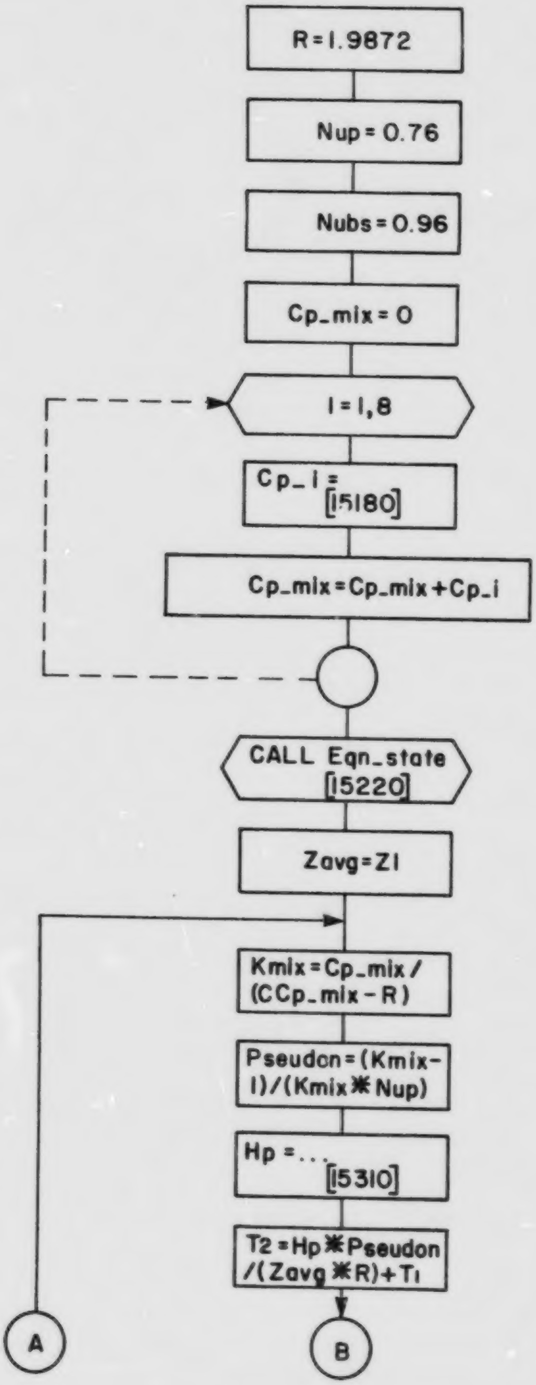

Figure A20. Flow chart for subprogramme "Compressor(Y(*),F,T1,T2,P1,P2,Hcomp." [], line number in programme listing.

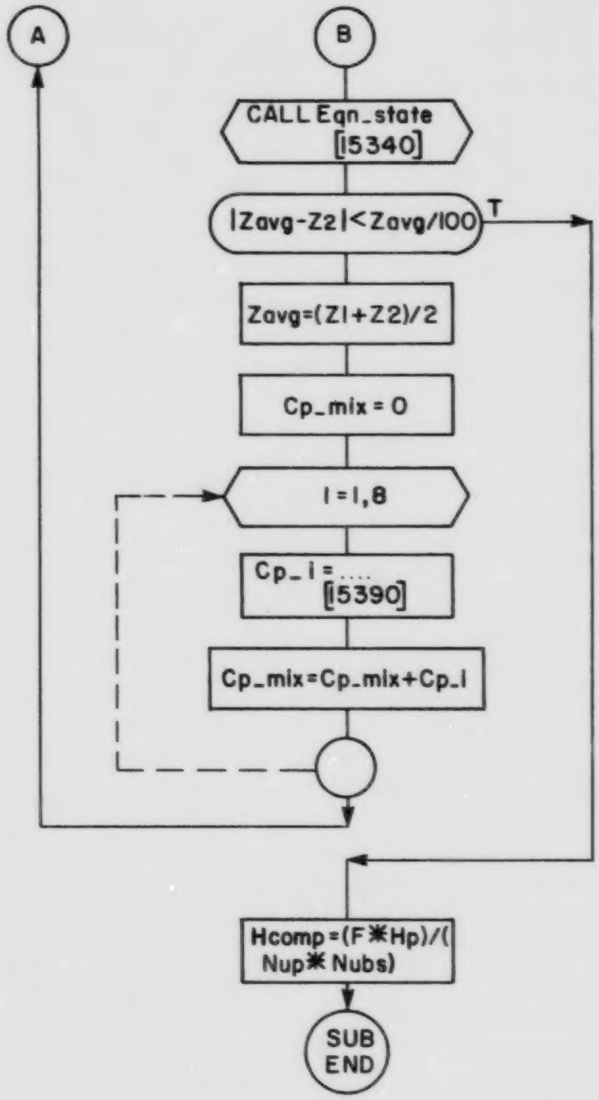

Figure A20. (Concluded).

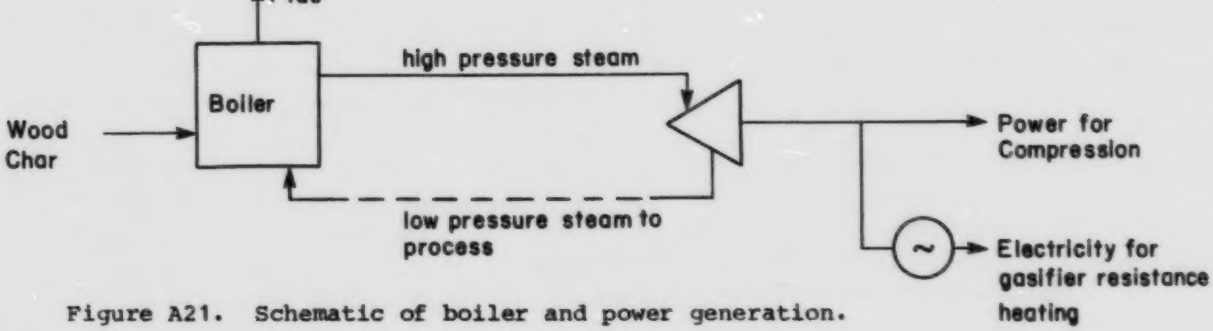
Flue
Boiler
Wood
Char
high pressure steam
low pressure steam to process
Power for Compression
~
Electricity for gasifier resistance heating

Figure A21. Schematic of boiler and power generation.

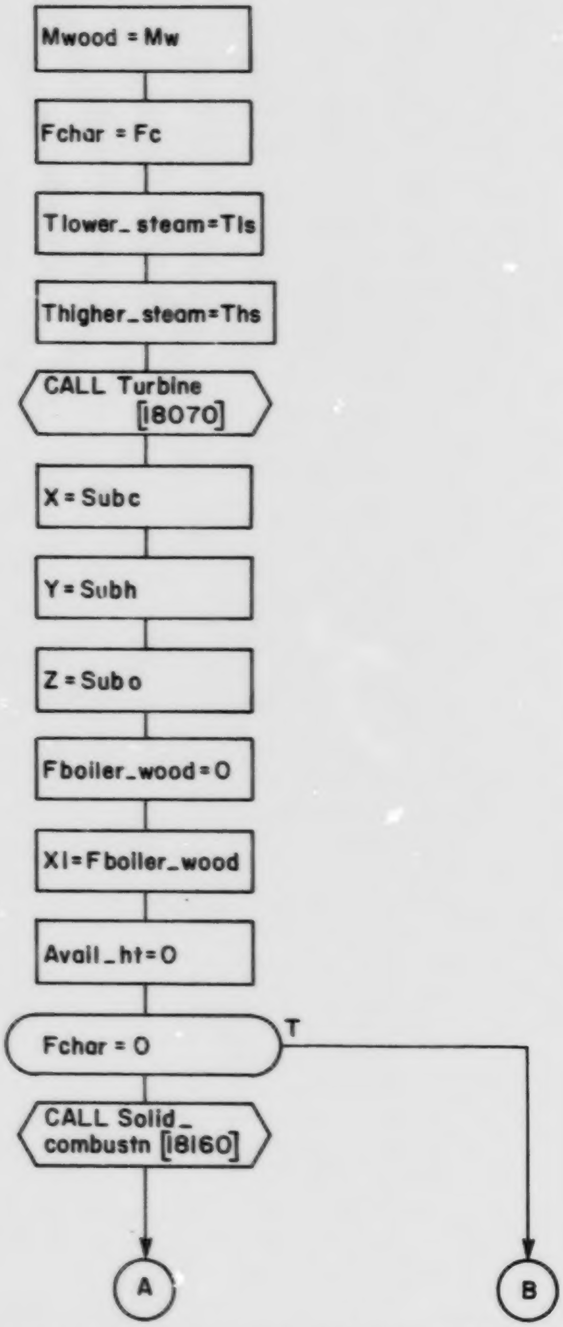

Figure A22. Flow chart for subprogramme "Boiler(Fboiler - wood,Mw,Mcwood,Fc,Mc_char,Subc,Subh,T1S,Ths,Comp_power,Turbine_eff,Boiler stack_O2,Hfwood,Avail_ht,Fst,Ext_ht,Fsteam)." [], line number in programme listing.

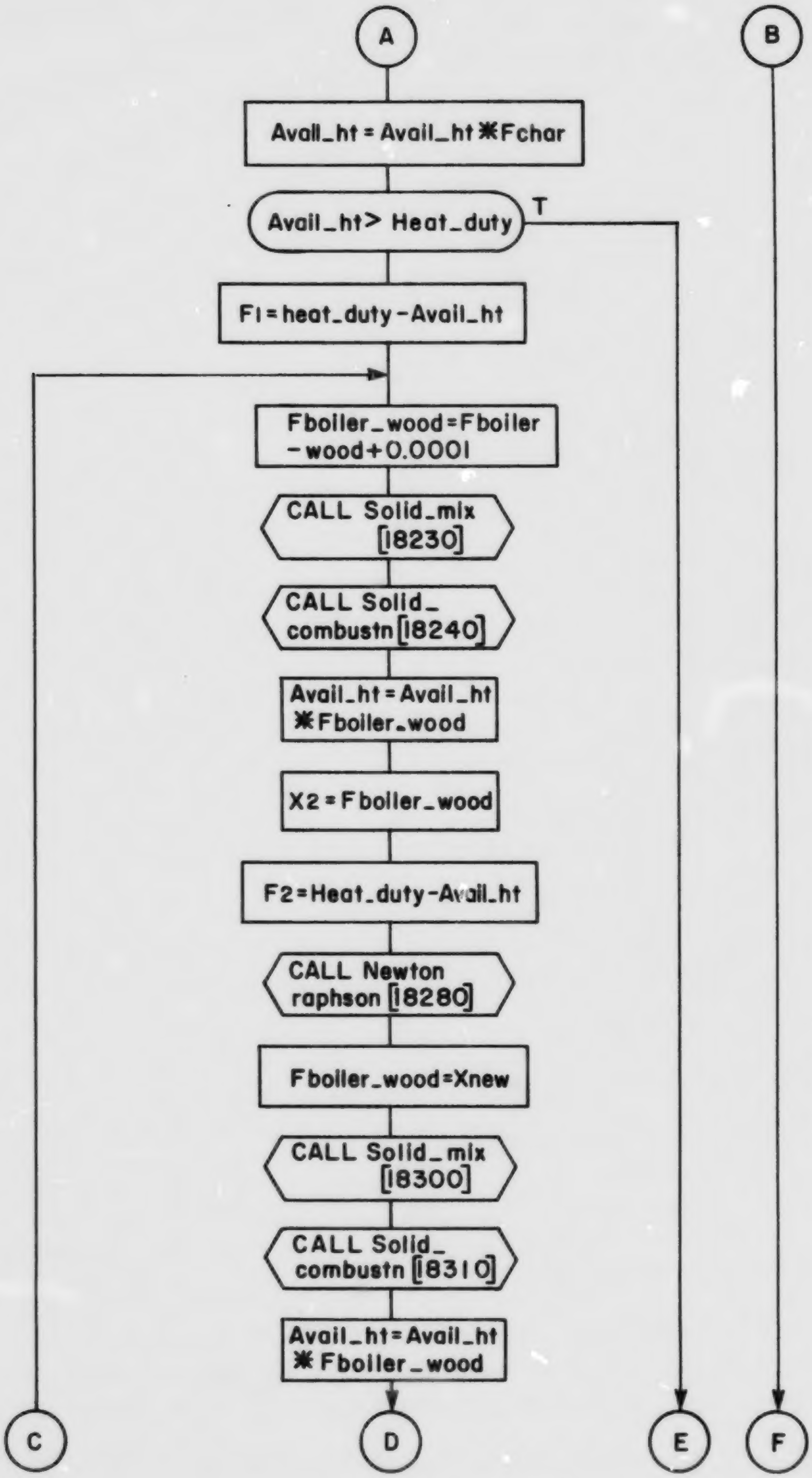
A
B
Avail_ht = Avail_ht * Fchar
Avail_ht > Heat_duty
T
F1 = heat_duty - Avail_ht
Fboiler_wood = Fboiler -wood + 0.0001
CALL Solid_mix [18230]
CALL Solid_combustn [18240]
Avail_ht = Avail_ht * Fboiler_wood
X2 = Fboiler_wood
F2 = Heat_duty - Avail_ht
CALL Newton raphson [18280]
Fboiler_wood = Xnew
CALL Solid_mix [18300]
CALL Solid_combustn [18310]
Avail_ht = Avail_ht * Fboiler_wood
C
D
E
F

Figure A22. (Continued).

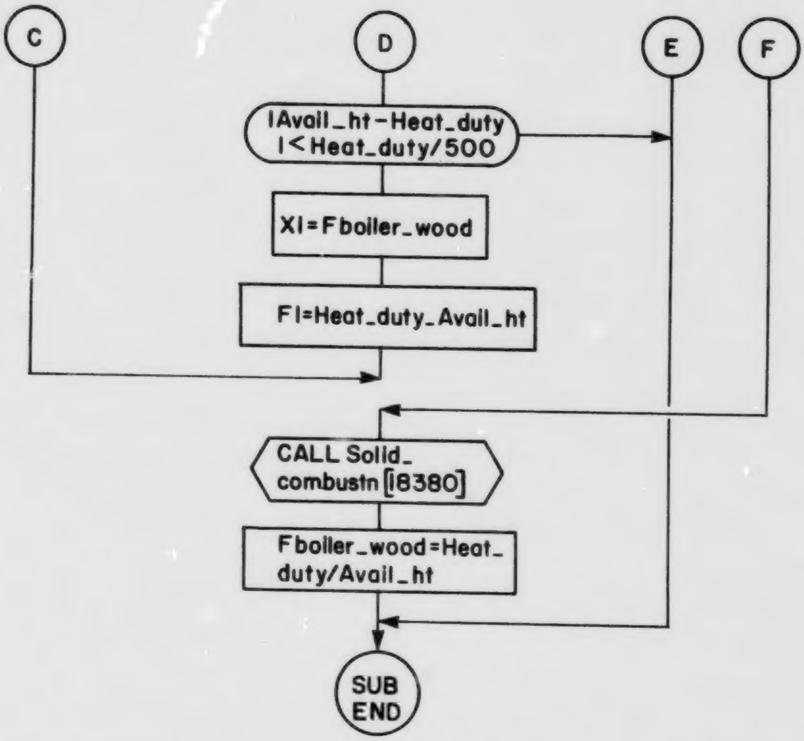

Figure A22. (Concluded).

production rate of the boiler given the total power requirements. "Solid mix(Fboiler wood,Mwood,=Mcwood,Fchar,Mc-char, Subc, Subh, Subo, X, Mc-new, Mw-new)" is used to determine the composition and moisture content of a mixed wood and char stream, given the characteristics of the two feed streams. "Solid_combustion(Tref,Texit,O2,X,Y,=Z,Mw,Mc,Heat form,Avail ht)" determines the available heat for the combustion of wet wood, given the stack O2 and temperature.

A11.0 PROCESS EFFICIENCY

A11.1 Efficiency(Ymm,Fm,Fwood dryer,Fwood boiler, Subc, Mwood, Hv wood, Anf,C conv,=First-law)

This subprogramme determines the overall carbon conversion for the process and the first law efficiency which is the ratio of the total heat of combustion of the methanol produced by the process to the total heat of combustion of the wood fed to the process.

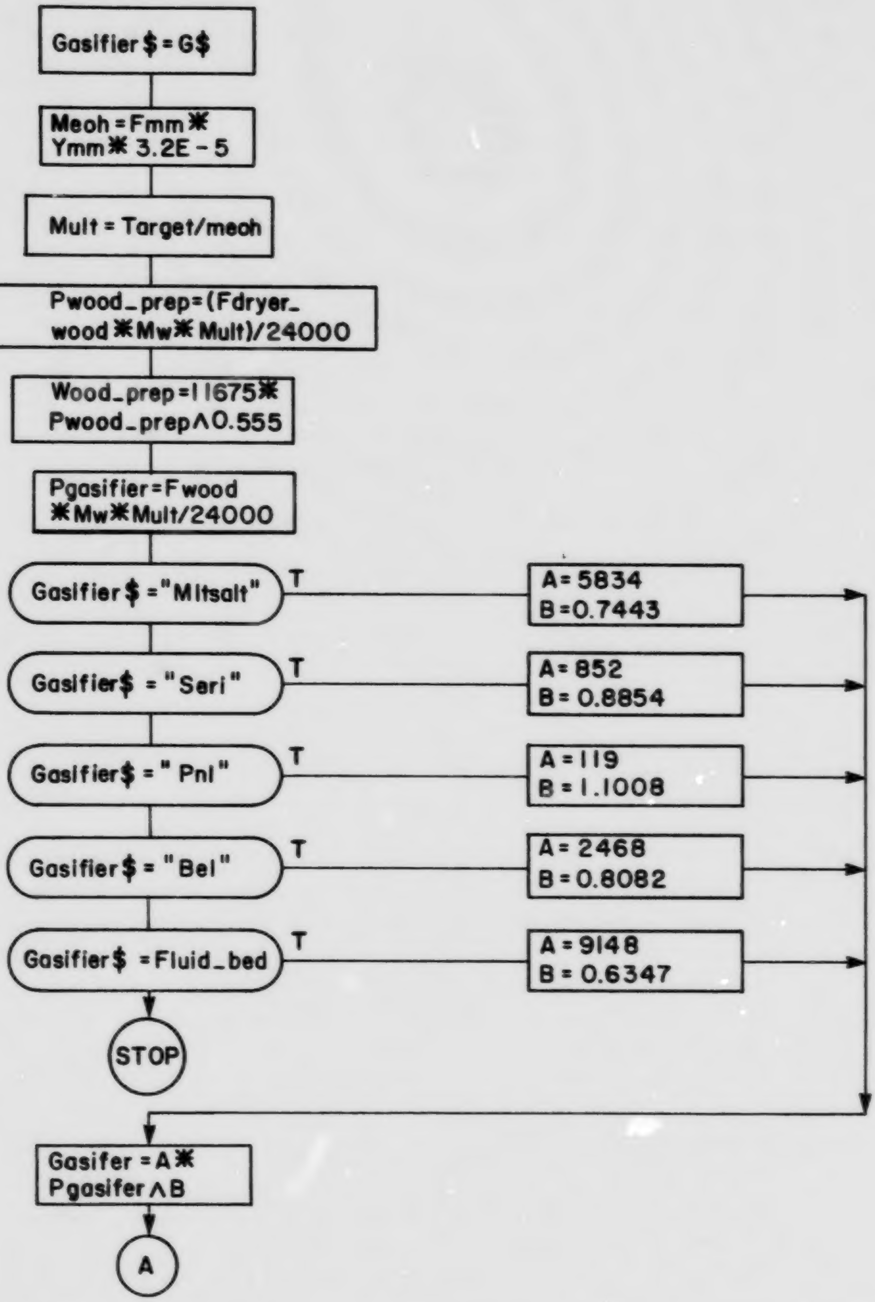

Figure A23. Flow chart for subprogramme "Plant_capital(Mw,Target, Fdryer wd,Fwood,Fgasin,Ygasin,Ffr,Yfr,Finco,Yinco,Foco,Yoco,Finacid,Yinacid,Ffacid,Yfacid,Fmm,Ymm,FO2,Power,Fsteam_boiler,G$)." [], line number in programme listing.

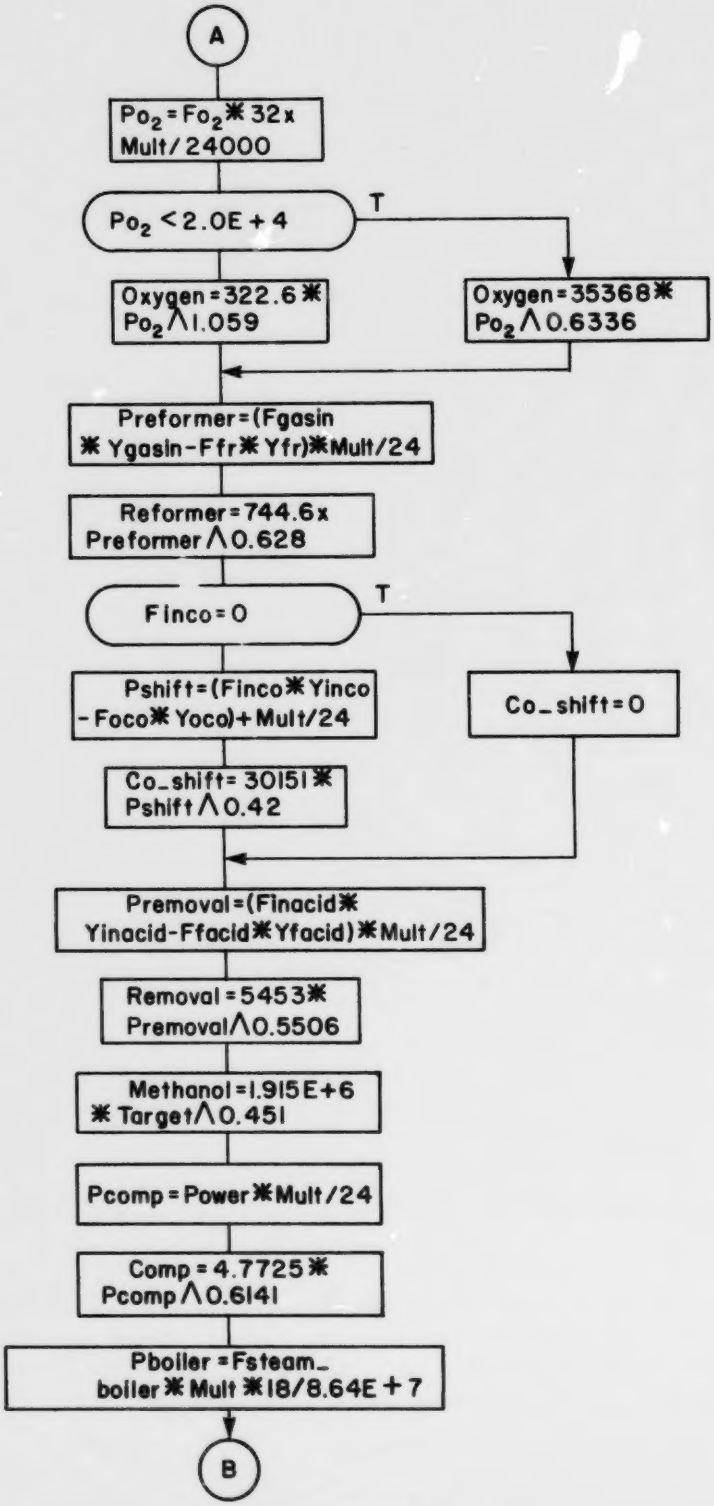
A
Po2 = Fo2 ✱ 32x Mult/24000
Po2 < 2.0E + 4
T
Oxygen = 322.6 ✱ Po2 Λ 1.059
Oxygen = 35368 ✱ Po2 Λ 0.6336
Preformer = (Fgasin ✱ Ygasin - Ffr ✱ Yfr) ✱ Mult/24
Reformer = 744.6x Preformer Λ 0.628
Finco = 0
T
Pshift = (Finco ✱ Yinco - Foco ✱ Yoco) + Mult/24
Co_shift = 0
Co_shift = 30151 ✱ Pshift Λ 0.42
Premoval = (Finacid ✱ Yinacid - Ffacid ✱ Yfacid) ✱ Mult/24
Removal = 5453 ✱ Premoval Λ 0.5506
Methanol = 1.915E+6 ✱ Target Λ 0.451
Pcomp = Power ✱ Mult/24
Comp = 4.7725 ✱ Pcomp Λ 0.6141
Pboiler = Fsteam_boiler ✱ Mult ✱ 18/8.64E + 7
B

Figure A23. (Continued).

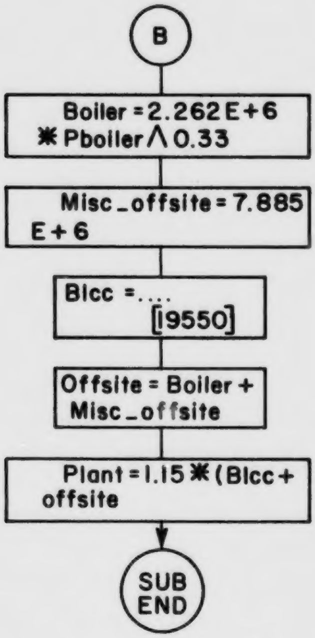
B
Boiler = 2.262E+6 ✱Pboiler∧0.33
Misc_offsite = 7.885 E+6
Blcc =....
[19550]
Offsite = Boiler + Misc_offsite
Plant = 1.15✱(Blcc+ offsite
SUB END

Figure A23. (Concluded).

A12.0 ECONOMICS

A12.1 Plant capital(Mw,Target,Fdryer wd,Fwood, Fgasin,Ygasin, Ffr,Yfr, Finco,=Yinco,Foco,Y oco,Finacid,Yinacid,Ffacid,Yfacid,Fmm,Ymm,Fo2, Power,Fsteam boiler,=G$)

The process unit capital costs are determined in this subprogramme and then combined to give the battery limit and offsite capital costs, from which the total plant capital cost is determined. The process flow chart for this subprogramme is shown in Figure A23.

A12.2 Operat_maint(Fboiler-wood,Fdryer wood,Mwood,Target,F mm,Ymm, Gasifier$)

The total operating cost which consists of labour, maintenance, raw material, and utility (process and cooling water) costs is determined with the subprogramme "Operat maint". The flow chart for this subprogramme is shown in Figure A24.

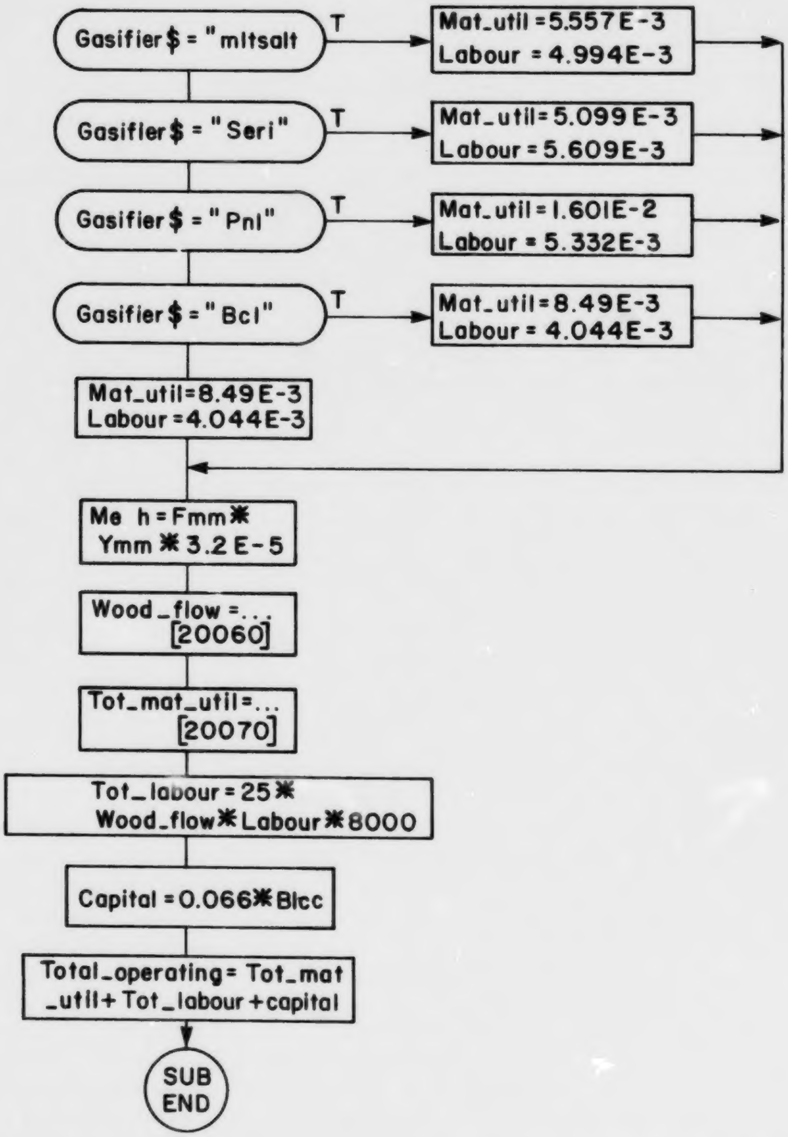

Figure A24. Flow chart for subprogramme "Operat_maint(Fboiler_wood,Fdryer_wood,Mwood,Target,Fmm,Ymm,Gasifier$)." [], line number in programme listing.

A12.3 Supply_price (Plant,Total operating,Target)

The methanol supply price is determined with this subprogramme given the plant capital cost, operating cost, discount factor, and plant life.

A13.0 MISCELLANEOUS SUBPROGRAMMES

A number of additional subprogrammes are used for data print out, storage, and retrieval. Further information may be obtained from the programme listing.

REFERENCE

Moffatt, J.M., and Anand, U.S. 1984. Molten Salt Technology for Wood to Syngas Conversion. Phase 2. Task 2. Final Report Technical Economic Assessment," National Research Council of Canada, Ottawa, Ontario Contract No. OSX82-0022 6.

APPENDIX B

PROCESS SIMULATION MODEL

B1. PROGRAMME LISTING

```
10     !MASS BALANCE FOR GAS PROCESSING (INDIRECT LIQUEFACTION)
20     !INPUT INITIAL GAS COMPOSITION
30     OPTION BASE 1
40    COM /Tp/ Tr1,Tr2,Pr,Tm1,Tm2,Pm
50    COM /Equilk/ Kgamref,K1r,K2r,F1r,F2r,Kgamshift,Kgam6,Kgam8,K1m,K2m,F1m,F2m
60    COM /Composition/ Yinr(8),Yfr(8),Yinco(8),Yfco(8),Yinacid(8),Yfacid(8),Yinm
(8),Yfm(8),Yrm(8),Ymm(2)
70    COM /Conversion/ Xref,Yref,Xmeth,Ymeth
80    COM /Flows/ Finr,Ffr,Finco,Ffco,Finacid,Ffacid,Finm,Ffm,Frm,Fmm,Fpm
90    COM /Eq2/ F2
100   COM /Eq1/ F1
110   COM /Rec/ Y,X
120   COM /Ks/ K1,K2
130   COM /Tpm/ T1,T2,P
140   COM /Ktest/ K1test,K2test
150   COM /Flow/ Fo,Fin,Fout,Fr,Fp,Fm
160   COM /Initial/ Yo(8),Yf(8),Yin(8),Yr(8),Ym(8)
170   COM /Element/ Co,Cp,Cme,Oo,Op,Ome,Ho,Hp,Hme
180   COM /Co_shift/ Tco,Pco,Kgamco,Fbyco,Youtco(8),Foutco,Fco_steam
190   COM /Acid_rem/ Yfco2,Yfh2o,Tacid_gas
200   COM /Reformer/ Steam,Methane,Ygasin(8),Fgasin,Ua,Ref_stack_o2
210   COM /Methanol/ Frstore,Yr_target,Indicator$[8]
220   COM /Data_storage/ A(19,8)
230   COM /Heat_capacity/ Coef(9,4)
240   COM /Temperature/ T(20)
250   COM /Energy/ Gf(9),Hf(9),Integral(8)
260   COM /Combustion/ Fcombgas,Stack_o2
270   COM /Critical/ Critical(2,8)
280   COM /Compression/ Hcomp(5,5)
290   COM /Wood/ Wood(8),Subc,Subh,Subo,Mwood,Hfwood
300   COM /Gasifier/ Fwood,Fsteam,Fchar,Fo2,Fh2o,Fcond,Fgas,Ygas(8),Fgasifier,Yga
sifier(8),Twood,Tsteam,Tgas,To2,Char_yield,Ext_ht_supply,Gasifier$[10]
310   COM /Dryer/ Ffdry_wood,Fdryer_wood,Tdryer,Dryer_stack_o2,Fevap
320   COM /Oxygen/ Power
330   COM /Boiler/ Fboiler_wood,Tlower_steam,Thigher_steam,Boiler_stack_o2,Turbin
e_eff,Avail_ht,Mc_char,Fsteam_boiler
340   COM /Efficiency/ C_conv,First_law
350   COM /Capital1/ Pwood_prep,Wood_prep,Pgasifier,Gasifier,Po2,Oxygen,Preformer
,Reformer,Pshift,Co_shift,Premoval,Removal,Methanol,Pcomp,Comp,Pboiler
360   COM /Capital2/ Boiler,Misc_offsite,Blcc,Offsite,Plant
370   COM /Operating/ Wood_cost,Tot_mat_util,Tot_labour,Capital,Total_operating
380   COM /Target_meth/ Target
390   COM /Price/ Supply_price,Interest,Years
400   COM Ytemp(8)
```

```
410  !                   ***WOOD CHARACTERISTICS***
420  !C,H,O,N,ASH,MC(TO GASIFIER):%; HHV:CAL/G;MC(TO DRYER):%
430  DATA 49.31,4.93,44.73,0.33,0.70,5.35,4718,50
440  !                   ***GASIFIER***
450  !TYPE OF GASIFIER (Seri,Mltsalt,Fluid_bed,Pnl,Bcl)
460  DATA "Mltsalt"
470  !                      Ygas(*) FROM GASIFIER, MOLE FRACTION
480  !                      CO,CO2,CH3OH,H2,H2O,CH4,N2,O2
490   DATA 0.2589,0.3511,0.000,0.2920,0.0000,0.0979,0.0000,0.0000
500   !                     FLOW FROM GASIFIER, M/t
510   !                     For normal operation use 1.0
520   DATA 1.00
530   !                     TGAS, 'C
540   DATA 850
550   !                    CHAR_YIELD, FRACTION DRY WOOD FEED, WT BASIS; TSTEAM, 'C
560   DATA 0.0649,288
570   !                     ***REFORMER***
580   !                     T(1):TEMPERATURE OF GAS TO REFORMER
590   DATA 250
600   !                     Tr1,Tr2,'C;Pr(ATM):DATA FOR REFORMER
610   DATA 850,850,20
620   !                      REFORMER STACK O2: FRACTION
630   DATA 0.02
640   !                     METHANE CONC IN OUTLET OF REFORMER
650   DATA 0.01
660   !                     Tm1,Tm2,'C;Pm(kP):DATA FOR METHANOL SYNTHESIS
670   DATA 250,250,5000
680   !                     K1r(STEAM REFORMING OF CH4)
690   DATA 3929
700   !                     KGAM6(CO TO CH3OH),KGAM8(INVERSE WATER GAS SHIFT):METHANOL
710   !                     KGAMREF (STEAM REFORMING OF CH4)
720   !                     EQUIL COEFFICIENT FORMED FROM ACTIVITY COEFF:FN OF T & P
730   DATA 0.78,0.62,1.00
740  !                    ***CO SHIFT***
750  !                    Tco('C),Pco(ATM),Kgamco
760  DATA 350,20,0.97
770  !                     ***ACID GAS REMOVAL***
780  !                     YFACID(CO2),YFACID(H2O):SPECIFY OUTLET CONDITIONS
790  !                     TACID_GAS, 'C
800  DATA 0.04,0.0,100
810  !                     ***METHANOL***
820  !                     FRSTORE:SPECIFY RECYCLE RATE RELATIVE TO INLET FLOW
830  !                     If concentration of CH4 in the recycle stream is to be set
840  !                     and recycle rate calculated based on this quantity then
850  !                     make changes indicated in Methanol subprogramme.
860  DATA 1.5
870  !                     ***PRETREAT:DRYER***
880  !                     TDRYER:STACK OUTLET TEMP, 'C;STACK_O2:FRACTION
890  DATA 150,0.05
900  !                     ***BOILER***
910  !     TLOWER_STEAM: TEMP STEAM AFTER TURBINE, 'C
920  !     THIGHER_STEAM: TEMP STEAM GENERATED BY BOILER AND FED TO TURBINE, 'C
```

```
930  !     BOILER_STACK_O2: FRACTION
940  !     TURBINE_EFF: TURBINE EFFICIENCY ,FRACTION
950  DATA 288,400,0.05,0.75
960  !                 ***SPECIFIC HEAT COEFFICIENTS***
970  !CO:
980  DATA 7.0852,-1.46753E-03,3.98378E-06,-1.6668E-09
990  !CO2:
1000 DATA 4.9727,1.6168E-02,-1.10921E-05,2.9243E-09
1010 !CH3OH:
1020 DATA 4.5489,2.1857E-02,-2.9075E-06,-1.92E-09
1030 !H2:
1040 DATA 6.73166,7.6678E-04,-7.9018E-07,5.03619E-10
1050 !H2O:
1060 DATA 7.79678,-1.78036E-04,3.46408E-06,-1.22932E-09
1070 !CH4:
1080 DATA 4.8723,1.07719E-02,5.47676E-06,-3.8375E-09
1090 !N2:
1100 DATA 7.20139,-1.9214E-03,4.1995E-06,-1.65998E-09
1110 !O2:
1120 DATA 6.34224,2.14122E-03,4.62397E-07,-6.00486E-10
1130 !C:GRAPHITE
1140 DATA 2.673,2.617E-03,-1.169E05,0
1150 !           *** HEAT OF FORMATION CAL/M***
1160 !       CO,CO2,CH3OH,H2,H2Og,CH4,N2,O2,H2OI
1170 DATA -26416,-94052,-48080,0,-57798,-17889,0,0,-68317
1180 !           *** FREE ENERGY OF FORMATION, 25'C:CAL/M***
1190 DATA -32808,-94260,-38620,0,-54635,-12140,0,0,-56690
1200 !             ***CRITICAL CONSTANTS***
1210 !                       **Tc**
1220 DATA 133,304.2,513.2,33.3,647.3,190.7,126.1,154.4
1230 !                       **Pc**
1240 DATA 34.5,72.8,78.7,12.8,217.7,45.8,33.5,49.7
1250 !                  ***************
1260 !             ****WOOD COST, $CAN/DRY Kg****
1270 DATA 2.5E-02
1280 !             ***METHANOL FLOW (TARGET): TONNE/D****
1290 DATA 500
1300 !           ***DATA FOR SUPPLY PRICE CALC***
1310 !            ***INTEREST (Discount Factor),FRACTION;YEARS****
1320 DATA 0.07,20
1330  READ Wood(*)
1340  READ Gasifier$
1350  READ Ygas(*)
1360  READ Fgas
1370  READ Tgas
1380  READ Char_yield,Tsteam
1390  READ T(1)
1400  READ Tr1,Tr2,Pr
1410  READ Ref_stack_o2
1420  READ Methane
1430  READ Tm1,Tm2,Pm
```

```
1440  READ K1r
1450  READ Kgam6,Kgam8,Kgamref
1460  READ Tco,Pco,Kgamco
1470  READ Yfco2,Yfh2o,Tacid_gas
1480  READ Frstore
1490  READ Tdryer,Dryer_stack_o2
1500  READ Tlower_steam,Thigher_steam,Boiler_stack_o2,Turbine_eff
1510  READ Coef(*)
1520  READ Hf(*)
1530  READ Gf(*)
1540  READ Critical(*)
1550  READ Wood_cost
1560  READ Target
1570  READ Interest,Years
1580  !____________________________________________________________
1590 Logic: !
1600      CALL Process_logic
1610  !____________________________________________________________
1620  END
1630  !****************************************************************
1640  SUB Equilibriumr(Yo(*),Fo)
1650 Equilibriumr: !
1660  !DETERMINE EQUILIBRIUM GAS COMPOSITION GIVEN TWO SIMULTANEOUS REACTIONS
1670  !INITIAL CONDITIONS:
1680  !YO(1):CO,YO(2):CO2,YO(3):CH3OH,YO(4):H2,YO(5):H2O,YO(6):CH4,YO(7):N2
1690  !TR1:TEMPERATURE OF FIRST REACTION, TR2:TEMPERATURE OF SECOND REACTION, P:
PRESSURE OF REACTOR
1700  !Y IS DETERMINED AS THE ROOT OF A POLYNOMIAL
1710  !A CRUDE ITERATIVE ALGORITHM IS USED TO ESTIMATE X
1720  !X=CH4(INIT)-CH4(FINAL), CONVERSION FOR STEAM REFORMING
1730  !Y=CO2(INIT)-CO2(FINAL), CONVERSION FOR WATER GAS SHIFT
1740  !F1 REFERS TO THE STEAM REFORMING OF METHANE
1750  !F1=CO*H2**3*P**2/(H2O*CH4)-K1=0 FOR EQUILIBRIUM
1760  !K1 IS THE EQUILIBRIUM CONSTANT FOR THE STEAM REFORMING REACTION
1770  !F2 REFERS TO THE WATER GAS SHIFT REACTION
1780  !F2=CO2*H2/(CO*H2O)-K2=0 FOR EQUILIBRIUM
1790  !K2 IS THE EQUILIBRIUM CONSTANT FOR THE WATER GAS SHIFT REACTION
1800  !NOTE THAT THE FUNCTION FOR DETERMINING X IS COMPLEX  AND HAS A HYPERBOLIC
 COMPONENT
1810  OPTION BASE 1
1820  INTEGER I,J
1830  !YF IS THE MOLE FRACTION AT THE OUTLET OF THE REACTOR
1840  COM /Approach/ Approachmx,Approachmk1,Approachmfr,Approachrx,Approachrk2,A
pproachry
1850  COM /Eq2/ F2
1860  COM /Eq1/ F1
1870  COM /Tp/ Tr1,Tr2,Pr,Tm1,Tm2,Pm
1880  COM /Ks/ K1,K2
1890  COM /Equilk/ Kgamref,K1r,K2r,F1r,F2r,Kgamshift,Kgam6,Kgam8,K1m,K2m,F1m,F2m
1900  COM /Composition/ Yinr(*),Yfr(*),Yinco(*),Yfco(*),Yinacid(*),Yfacid(*),Yin
m(*),Yfm(*),Yrm(*),Ymm(*)
1910  COM /Conversion/ Xref,Yref,Xmeth,Ymeth
```

```
1920  COM /Flows/ Finr,Ffr,Finco,Ffco,Finacid,Ffacid,Finm,Ffm,Frm,Fmm,Fpm
1930  COM /Gasifier/ Fwood,Fsteam,Fchar,Fo2,Fh2o,Fcond,Fgas,Ygas(*),Fgasifier,Yg
asifier(*),Twood,Tsteam,Tgas,To2,Char_yield,Ext_ht_supply,Gasifier$
1940  K1=K1r
1950  T=Tr1+273
1960  CALL Kshift(T,K2r)
1970  K2=K2r
1980  Rcounter=.999995*Yo(6)
1990 Rtryagain: !
2000  X=Rcounter
2010  IF (X>0) THEN GOTO Bypass0
2020  PRINT "REFORMER EQUIL CALC DOES NOT CONVERGE"
2030  PRINT "X<0"
2040  PRINT "PROGRAMME TERMINATED"
2050  STOP
2060 Bypass0: !
2070  !DETERMINE Y THAT CORRESPONDS TO X
2080  CALL Recursionr(Yo(*),X,Y,K2)
2090  CALL Equil1r(Yo(*),X,Y,K1)
2100  IF (X1<0) THEN X1=0
2110  J=1
2120 Repeat40: !
2130  Xn=X
2140  F1n=F1
2150  IF (F1<0) THEN GOTO Test
2160  Test1$="B"
2170  GOTO Skip
2180 Test: !
2190  Test1$="A"
2200 Skip: !
2210  X=Xn-.10*Rcounter/J
2220  CALL Recursionr(Yo(*),X,Y,K2)
2230  CALL Equil1r(Yo(*),X,Y,K1)
2240  IF (F1<0) THEN GOTO Test1
2250  Test2$="B"
2260  GOTO Skip2
2270 Test1: !
2280  Test2$="A"
2290 Skip2: !
2300  !INTRODUCE CONDITIONAL TO PREVENT UNDERFLOW ERROR FOR SMALL VALUES OF x
2310  IF (ABS(F1)<K1/1000) THEN GOTO Rokay
2320  IF (ABS(Xn-X)<1.E-5) THEN GOTO Finish
2330  IF (ABS(Xn-X)<X/5000) THEN GOTO Finish
2340  IF (Test1$=Test2$) THEN GOTO Repeat40
2350  J=J+1
2360  GOTO Skip
2370 Finish: !
2380  FOR I=1 TO 7
2390  IF (Yf(I)<-1.0E-6) THEN GOTO Rbypass3
2400  NEXT I
2410  !CONDITIONAL ADDED TO ELIMINATE FALSE ROOTS DUE TO HYPERBOLICS
```

```
2420  GOTO Rokay
2430 Rbypass3: !
2440  PRINT "YF(";I;")";Yf(I)
2450  PRINT "CONVERGENCE TO WRONG VALUE OF X"
2460  STOP
2470 Rokay: !
2480  CALL Equil1r(Yo(*),X,Y,K1)
2490  CALL Equil2r(Yo(*),X,Y,K2)
2500  F1r=F1
2510  F2r=F2
2520  Den=1+2*X
2530  Yfr(1)=(Yo(1)+X+Y)/Den
2540  Yfr(2)=(Yo(2)-Y)/Den
2550  Yfr(6)=(Yo(6)-X)/Den
2560  Yfr(4)=(Yo(4)+3*X-Y)/Den
2570  Yfr(5)=(Yo(5)-X+Y)/Den
2580  Yfr(3)=Yo(3)/Den
2590  Yfr(7)=Yo(7)/Den
2600  Ffr=Fo*Den
2610  Xref=X
2620  Yref=Y
2630  SUBEND
2640  !____________________________
2650  SUB Recursionr(Yo(*),X,Y,K2)
2660 Recursionr: !
2670  !DETERMINE Y FOR GIVEN X
2680  COM /Approach/ Approachmx,Approachmk1,Approachmfr,Approachrx,Approachrk2,A
pproachry
2690  COM /Eq1/ F1
2700  Alpha1=Yo(1)+X
2710  Alpha2=Yo(5)-X
2720  Alpha3=Yo(4)+3*X
2730  Alpha4=K2-1
2740  Beta=-(K2*(Yo(2)+Alpha3)+Alpha2+Alpha1)
2750  Gamma=K2*Yo(2)*Alpha3-Alpha1*Alpha2
2760  Square=Beta^2-4*Alpha4*Gamma
2770  IF (Square<0) THEN GOTO Problem
2780  Sqrroot=Square^.5
2790  Y=(-Beta-Sqrroot)/(2*Alpha4)
2800  GOTO Finishy
2810 Problem: !
2820  PRINT "REFORMER (RECURSIONR): SQUARE < 0"
2830  STOP
2840 Finishy: !
2850  SUBEND
2860  !_______________________
2870  SUB Equil1r(Yo(*),X,Y,K1)
2880  !THIS SUB DETERMINES THE DIFFERENCE BETWEEN THE SPECIFIED K FOR THE STEAM
REFORMING OF CH4 AND THE CALC VALUE
2890 Equil1r: !
2900  !FIRST EQUILIBRIUM EQUATION
```

```
2910  COM /Tp/ Tr1,Tr2,Pr,Tm1,Tm2,Pm
2920  COM /Eq1/ F1
2930  F1=(Yo(1)+Y+X)*(Yo(4)-Y+3*X)^3*Pr^2
2940  F1=F1/((Yo(6)-X)*(Yo(5)+Y-X)*(1+2*X)^2)-K1
2950  SUBEND
2960  !_______________________
2970  SUB Equil2r(Yo(*),X,Y,K2)
2980  !THIS SUB DETERMINES THE DIFFERENCE BETWEEN THE SPECIFIED K OF THE WATER G
AS SHIFT AND THE CALC VALUE
2990 Equil2r: !
3000  COM /Tp/ Tr1,Tr2,Pr,Tm1,Tm2,Pm
3010  COM /Eq2/ F2
3020  F2=((Yo(1)+Y+X)*(Yo(5)+Y-X))/((Yo(2)-Y)*(Yo(4)-Y+3*X))-K2
3030  SUBEND
3040  !_____________________________________________________________________________
3050  SUB Equilibrium(Yin(*);Fin,Yf(*),Fout)
3060 Equilibrium: !
3070  !PRINT "EQUILIBRIUM FOR THE SYNTHESIS OF METHANOL"
3080  !METHANOL EQUILIBRIUM CALCULATIONS,SIMILAR TO METHANOL BUT INVERSE OF THE
WATER GAS SHIFT REACTION USED AS IN KIRK OTHMER,CH4&N2 ARE INCLUDED HERE**
3090  !A CRUDE ITERATIVE ALGORITHM IS USED TO ESTIMATE Y
3100  !A CRUDE ITERATIVE ALGORITHM IS USED TO ESTIMATE X
3110  !X=CH3OH(FINIAL)-CH3OH(INITIAL),CONVERSION FOR METHANOL FORMATION
3120  !Y=(CO2(INIT)-CO2(FINAL),CONVERSION FOR THE WATER GAS SHIFT REACTION
3130  !F1 REFERS TO THE INVERSE OF THE WATER GAS SHIFT REACTION
3140  !F1=CO*H2O/(CO2*H2)-K2=0 FOR EQUILIBRIUM; FOR GIVEN X,Y IS CALCULATED AS R
OOT OF POLYNOMIAL
3150  !K2 IS THE EQUILIBRIUM CONSTANT FOR THE WATER GAS SHIFT REACTION
3160  !F2 REFERS TO THE METHANOL SYNTHESIS REACTION FROM CO
3170  !F2=CH3OH/(CO*H2^2)-K1=0 FOR EQUILIBRIUM
3180  !K1 IS THE EQUILIBRIUM CONSTANT FOR THE METHANOL SYNTHESIS REACTION
3190  !NOTE THAT THE FUNCTION FOR DETERMINING X IS HYPERBOLIC
3200  !SUBPROGRAM RECURSIONB IS A NEWTON RAPHSON ITERATIVE PROCEDURE BUT IS NOT
EMPLOYED HERE
3210  !DETERMINE EQUILIBRIUM GAS COMPOSITION GIVEN TWO SIMULTANEOUS REACTIONS
3220  OPTION BASE 1
3230  INTEGER I,J
3240  COM /Rec/ Y,X
3250  COM /Eq2/ F2
3260  COM /Eq1/ F1
3270  COM /Tpm/ T1,T2,P
3280  COM /Ks/ K1,K2
3290  COM /Ktest/ K1test,K2test
3300  COM /Composition/ Yinr(*),Yfr(*),Yinco(*),Yfco(*),Yinacid(*),Yfacid(*),Yin
m(*),Yfm(*),Yrm(*),Ymm(*)
3310  COM /Tp/ Tr1,Tr2,Pr,Tm1,Tm2,Pm
3320  COM /Equilk/ Kgamref,K1r,K2r,F1r,F2r,Kgamshift,Kgam6,Kgam8,K1m,K2m,F1m,F2m
3330  T1=Tm1
3340  T2=Tm2
3350  P=Pm
3360  T=T1+273
```

```
3370  Ka6=9.74E-5*EXP(21.225+9143.6/T-7.492*LOG(T)+4.076E-3*T-7.161E-8*T^2)
3380  K1=Ka6*P^2/Kgam6
3390  K1m=K1
3400  CALL Kshift(T,Ka8)
3410  K2=Ka8/Kgam8
3420  K2m=K2
3430  Counter=.05*(Yin(1)+Yin(2))
3440  J=1
3450  X1=0
3460  CALL Recursion(Yin(*),X1,Y,K2)
3470  CALL Equil2(X1,Y,Yin(*))
3480  CALL Sign(F2,Test1$)
3490  F21=F2
3500  Xn=Counter/J
3510 Repeat40: !
3520  CALL Recursion(Yin(*),Xn,Y,K2)
3530  CALL Equil2(Xn,Y,Yin(*))
3540  CALL Sign(F2,Test2$)
3550  F2n=F2
3560  IF (ABS(F2)<K1/1000) THEN GOTO Okay
3570  IF (ABS(Xn-X1)<Xn/1000) THEN GOTO Okay
3580  IF (Xn>.999*(Yin(1)+Yin(2))) THEN GOTO Trouble
3590  IF (Test1$=Test2$) THEN GOTO Repeat1
3600  J=J+1
3610  Xn=X1+Counter/J
3620  GOTO Repeat40
3630 Repeat1: !
3640  X1=Xn
3650  F21=F2
3660 Repeat2: !
3670  Xn=Xn+Counter/J
3680  IF (Xn<Yin(1)+Yin(2)) THEN GOTO Repeat40
3690  J=J+1
3700  GOTO Repeat2
3710 Trouble: !
3720  PRINT "X NOT CONVERGING"
3730  PRINT "METHANOL SIMULATION TERMINATED"
3740  STOP
3750 Okay: !
3760  X=Xn
3770  IF (Yin(2)-Y=0) THEN GOTO Denbypass
3780  CALL Equil1(X,Y,Yin(*))
3790 Denbypass: !
3800  CALL Equil2(X,Y,Yin(*))
3810  K2test=F1+K2
3820  K1test=F2+K1
3830  CALL Yfmeoh_co(X,Y,Yin(*),Fin,Yf(*),Fout)
3840  SUBEND
3850  !______________________________
3860  SUB Recursion(Yo(*),X,Y,K)
3870 Recursionm: !
```

```
3980  !PRINT "RECURSION"
3850  !DETERMINE Y FOR GIVEN X
3900  COM /Eq1/ F1
3910  Galpha=Yo(1)-X
3920  Gbeta=Yo(4)-2*X
3930  Ep1=K-1
3940  Ep2=-(K*(Yo(2)+Gbeta)+(Galpha+Yo(5)))
3950  Ep3=K*Yo(2)*Gbeta-Galpha*Yo(5)
3960  Squart=(Ep2^2-4*Ep1*Ep3)
3970  IF (Squart>0) THEN GOTO Sq
3980  PRINT "SQUART<0"
3990  STOP
4000 Sq: !
4010  Squart=Squart^.5
4020  Y=(-Ep2-Squart)/(2*Ep1)
4030  SUBEND
4040  !_______________________
4050  SUB Equil1(X,Y,Yin(*))
4060  !THIS SUB CALC THE DIFFERENCE IN THE SPECIFIED VALUE OF K2 FOR THE *INVERS
E* WATER GAS SHIFT REACTION AND THE CALC VALUE
4070 Equil1m: !
4080  !PRINT "EQUIL1"
4090  !FIRST EQUILIBRIUM EQUATION
4100   COM /Tpm/ T1,T2,P
4110  COM /Eq1/ F1
4120  COM /Ks/ K1,K2
4130  F1=(Yin(1)-X+Y)*(Yin(5)+Y)/((Yin(2)-Y)*(Yin(4)-Y-2*X))-K2
4140  SUBEND
4150  !_______________________
4160  SUB Equil2(X,Y,Yin(*))
4170  !THIS SUB CAL THE DIFFERENCE BETWEEN THE SPECIFIED VALUE FOR K1 FOR THE SY
NTHESIS OF CH3OH FROM CO AND THE CALC VALUE
4180 Equil2m: !
4190   COM /Tpm/ T1,T2,P
4200  COM /Eq2/ F2
4210  COM /Ks/ K1,K2
4220  F2=(Yin(3)+X)*(1-2*X)^2/((Yin(1)-X+Y)*(Yin(4)-Y-2*X)^2)-K1
4230  SUBEND
4240  !
4250  SUB Methanol(Yinput(*),Finput)
4260 Methanol: !
4270  ! METHANOL SYNTHESIS MASS BALANCE
4280  ! EQUILIBRIUM MODEL
4290  INTEGER I,J
4300   COM /Rec/ Y,X
4310   COM /Eq2/ F2
4320   COM /Eq1/ F1
4330   COM /Tp/ Tr1,Tr2,Pr,Tm1,Tm2,Pm
4340   COM /Equilk/ Kqamref,K1r,K2r,F1r,F2r,Kqamshift,Kqam6,Kqam8,K1m,K2m,F1m,F2
m
4350   COM /Composition/ Yinr(*),Yfr(*),Yinco(*),Yfco(*),Yinacid(*),Yfacid(*),Yi
nm(*),Yfm(*),Yrm(*),Ymm(*)
```

```
4360   COM /Conversion/ Xref,Yref,Xmeth,Ymeth
4370   COM /Flows/ Finr,Ffr,Finco,Ffco,Finacid,Ffacid,Finm,Ffm,Frm,Fmm,Fpm
4380   COM /Methanol/ Frstore,Yr target,Indicator$[8]
4390    DIM Yrorig(7)
4400    FOR I=1 TO 7
4410    Yo(I)=Yinput(I)
4420    NEXT I
4430    Fo=Finput
4440    !CHECK THAT SPECIFICATIONS FOR SYNGAS STREAM ARE CORRECT
4450    CALL Normalize(Yo(*),Fo)
4460    !IF CH4 CONCENTRATION IS TO BE SPECIFIED IN RECYCLE THEN GIVE VALUE FOR
YR TARGET AND SET INDICATOR$ TO INERT
4470    Yr target=.075
4480    Indicator$="INERT"
4490    !SPECIFY INITIAL RECYCLE FLOW
4500    Fr=0
4510    Fp=0
4520    FOR I=1 TO 7
4530    Yr(I)=0
4540    NEXT I
4550    Flag!$="A"
4560 Mrepeat:   !
4570    Frcheck=Fr
4580    Fin=Fo+Fr
4590    FOR I=1 TO 7
4600    Yin(I)=(Fo*Yo(I)+Fr*Yr(I))/Fin
4610    NEXT I
4620    CALL Equilibrium(Yin(*),Fin,Yf(*),Fout)
4630    CALL Purification(Yf(*),Fout,Ym(*),Fm,Yr(*),Fr)
4640    IF (Indicator$="INERT") THEN GOTO Inert1
4650    !DETERMINE RECYCLE FLOW RATE
4660    IF (Fr-Frstore*Finput>0) THEN GOTO Deterpurge
4670    GOTO Mrepeat
4680 Deterpurge:   !
4690     Fp=Fr-Frstore*Finput
4700     Fr=Fr-Fp
4710     IF (ABS(Fp-Fo*Yo(6)/Yr(6))<Fp/100) THEN GOTO Mfinish
4720     GOTO Mrepeat
4730 Inert1:    !
4740    IF (Flag!$="B") THEN GOTO Inert2
4750    IF (Yr target-Yr(6)>Yr target/4) THEN GOTO Mrepeat
4760    Flag!$="B"
4770 Inert2:   !
4780    Fp=Yo(6)*Fo/Yr target
4790    Fr=Fr-Fp
4800    IF (ABS(Yr target-Yr(6))>Yr target/100) THEN GOTO Mrepeat
4810 Mfinish:   !
4820    FOR I=1 TO 7
4830    Yinm(I)=Yin(I)
4840    Yfm(I)=Yf(I)
4850    Yrm(I)=Yr(I)
```

```
4860    NEXT I
4870    FOR I=1 TO 2
4880    Ymm(I)=Ym(I)
4890    NEXT I
4900    Xmeth=X
4910    Ymeth=Y
4920    Finm=Fin
4930    Ffm=Fout
4940    Frm=Fr
4950    Fpm=Fp
4960    Fmm=Fm
4970    F1m=F1
4980    F2m=F2
4990    SUBEND
5000    !
5010    SUB Purification(Yf(*),Fout,Ym(*),Fm,Yr(*),Fr)
5020 Purification:   !
5030    DIM Ni(7)
5040    INTEGER I,J
5050    !ASSUME 100% RECOVERY OF METHANOL AND 100% REMOVAL OF WATER IN THE PURIF
ICATION
5060    !DETERMINE CHARACTERISTICS OF METHANOL PURGE STREAM FM
5070    Fm=Fout*(Yf(3)+Yf(5))
5080    Ym(1)=Fout*Yf(3)/Fm
5090    Ym(2)=Fout*Yf(5)/Fm
5100    !DETERMINE GAS STREAM COMPOSITION
5110    FOR I=1 TO 7
5120    Ni(I)=Fout*Yf(I)
5130    NEXT I
5140    Ni(3)=0
5150    Ni(5)=0
5160    Fr=0
5170    FOR I=1 TO 7
5180    Fr=Fr+Ni(I)
5190    NEXT I
5200    FOR I=1 TO 7
5210    Yr(I)=Ni(I)/Fr
5220    NEXT I
5230    SUBEND
5240    !
5250    SUB Normalize(Yo(*),Fo)
5260 Normalize:   !
5270    Frstore=0
5280    FOR I=1 TO 7
5290    Frstore=Frstore+Yo(I)*Fo
5300    NEXT I
5310    FOR I=1 TO 7
5320    Yo(I)=Yo(I)*Fo/Frstore
5330    NEXT I
5340    Fo=Frstore
5350    SUBEND
```

```
5360    !
5370    SUB Elementbal(Yo(*),Yr(*),Ym(*))
5380 Elementbal:   !
5390    !ELEMENTBAL IS USED IN THE PRINT STATEMENT FOR THE METHANOL SYNTHESIS
5400    !THIS SUB DETERMINES FOR THE INLET, PRODUCT AND METHANOL STREAMS THE MOL
ES OF EACH ELEMENT PER MOLE FLOWING
5410    COM /Element/ Co,Cp,Cme,Oo,Op,Ome,Ho,Hp,Hme
5420    Co=Yo(1)+Yo(2)+Yo(3)+Yo(6)
5430    Cp=Yr(1)+Yr(2)+Yr(3)+Yr(6)
5440    Cme=Ym(1)
5450    Oo=Yo(1)+2*Yo(2)+Yo(3)+Yo(5)
5460    Op=Yr(1)+2*Yr(2)+Yr(3)+Yr(5)
5470    Ome=Ym(1)+Ym(2)
5480    Ho=2*(Yo(4)+Yo(5))+4*(Yo(3)+Yo(6))
5490    Hp=2*(Yr(4)+Yr(5))+4*(Yr(3)+Yr(6))
5500    Hme=4*Ym(1)+2*Ym(2)
5510    SUBEND
5520    !
5530    SUB Kshift(T,Kinvshift)
5540    !DETERMINE THE EQUIL CONSTANT FOR THE INVERSE OF THE WATER GAS SHIFT REAC
TION
5550 Kshift:  !
5560    Kinvshift=EXP(13.148-5639.5/T-1.077*LOG(T)-5.44E-4*T+1.125E-7*T^2+49170/T
^2)
5570    SUBEND
5580    !
5590    SUB Prtmethanol(Yo(*),Fo)
5600 Prtmethanol:  !
5610    COM /Tp/ Tr1,Tr2,Pr,Tm1,Tm2,Pm
5620    COM /Equilk/ Kpamref,K1r,K2r,F1r,F2r,Kpamshift,Kpam6,Kpam8,K1m,K2m,F1m,F2
m
5630    COM /Composition/ Yinr(*),Yfr(*),Yinco(*),Yfco(*),Yinacid(*),Yfacid(*),Yi
nm(*),Yfm(*),Yrm(*),Ymm(*)
5640    COM /Conversion/ Xref,Yref,Xmeth,Ymeth
5650    COM /Flows/ Finr,Ffr,Finco,Ffco,Finacid,Ffacid,Finm,Ffm,Frm,Fmm,Fpm
5660 ! COM /Gasifier/ Fwood,Fsteam,Fchar,Fo2,Fh2o,Fcond,Fgas,Ygas(*),Fgasifier,Y
gasifier(*),Twood,Tsteam,Tgas,To2,Char yield,Ext ht supply
5670    COM /Element/ Co,Cp,Cme,Oo,Op,Ome,Ho,Hp,Hme
5680    COM /Methanol/ Frstore,Yr target,Indicator$[8]
5690 PRINT "METHANOL SYNTHESIS"
5700 PRINT "TEMP,°C=";Tm1
5710 PRINT "PRESS, kPa=";Pm
5720 PRINT "CONVERSIONS:"
5730 PRINT USING "2X,32A,2D.4D";"OVERALL C (BASED ON CO AND CO2):",Fmm*Ymm(1)/(F
o*(Yo(1)+Yo(2)+Yo(3)))
5740 PRINT USING "2X,35A,2D.4D,2X,7A,2D.4D,1A";"CO (BASED ON PROC UNIT INLET COM
P):",(Xmeth-Ymeth)/Yo(1),"(Xmeth=",Xmeth,")"
5750!PRINT USING "2X,35A,2D.4D,2X,7A,2D.4D,1A";"CO2 (BASED ON PROC UNIT INLET CO
MP):",Ymeth/Yo(2),"(Ymeth=",Ymeth,")"
5760 PRINT USING "7A,2X,14A,2D.3D";"TARGET:","RECYCLE RATIO=",Frstore
5770 PRINT USING "9X,16A,2D.4D";"CH4 CONC (INERT)",Yr target
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5790 PRINT USING "2X,12A,1X,10A";"TARGET USED:",Indicator$
5790 PRINT USING "14X,9A,9A,9A,9A,9A";"YO","Yin","Yout","Yr","Ym"
5800 PRINT USING "10A,2D.4D,2X,2D.4D,2X,2D.4D,2X,2D.4D";"CO:",Yo(1),Yinm(1),Yfm(
1),Yrm(1)
5810 PRINT USING "10A,2D.4D,2X,2D.4D,2X,2D.4D,2X,2D.4D";"CO2:";Yo(2),Yinm(2),Yfm
(2),Yrm(2)
5820 PRINT USING "10A,2D.4D,2X,2D.4D,2X,2D.4D,2X,2D.4D,2X,2D.4D";"CH3OH:";Yo(3),
Yinm(3),Yfm(3),Yrm(3),Ymm(1)
5830 PRINT USING "10A,2D.4D,2X,2D.4D,2X,2D.4D,2X,2D.4D";"H2:";Yo(4),Yinm(4),Yfm(
4),Yrm(4)
5840 PRINT USING "10A,2D.4D,2X,2D.4D,2X,2D.4D,2X,2D.4D,2X,2D.4D";"H2O:";Yo(5),Yi
nm(5),Yfm(5),Yrm(5),Ymm(2)
5850 PRINT USING "10A,2D.4D,2X,2D.4D,2X,2D.4D,2X,2D.4D";"CH4:",Yo(6),Yinm(6),Yfm
(6),Yrm(6)
5860 PRINT USING "10A,2D.4D,2X,2D.4D,2X,2D.4D,2X,2D.4D";"N2:",Yo(7),Yinm(7),Yfm(
7),Yrm(7)
5870 PRINT USING "10A,2D.4D,2X,2D.4D,2X,2D.4D,2X,2D.4D,2X,2D.4D";"FLOW,M/t:",Fo,
Finm,Ffm,Frm,Fmm
5880 PRINT USING "6X,6A,2X,2D.4D,2X,25A";"PURGE:",Fpm,"(COMP SAME AS RECYCLE)"
5890 PRINT "CHECK FOR EQUIL CONVERGENCE, COMPARE EQUIL CONST"
5900 PRINT TAB(2);"SPECIFIED:"
5910 PRINT USING "2X,5A,4D.4D,2X,5A,4D.4D";"K1m=",K1m,"K2m=",K2m
5920 PRINT TAB(2);"CALC FROM COMP:"
5930 PRINT USING "2X,5A,4D.4D,2X,5A,4D.4D";"K1m=",F2m+K1m,"K2m=",F1m+K2m
5940 PRINT "CHECK FOR PURGE BALANCE:"
5950 PRINT USING "13X,3A,7X,2A";"CH4","N2"
5960 PRINT USING "10A,2D.4D,3X,2D.4D";"IN:",Yo(6)*Fo,Yo(7)*Fo
5970 PRINT USING "10A,2D.4D,3X,2D.4D";"OUT:",Yrm(6)*Fpm,Yrm(7)*Fpm
5980 PRINT "CHECK FOR OVERALL ELEMENT BALANCE"
5990 PRINT USING "13X,A,9X,A,9X,A";"C","O","H"
6000 !
6010 CALL Elementbal(Yo(*),Yrm(*),Ymm(*))
6020 !
6030 PRINT USING "10A,2D.4D,3X,2D.4D,3X,2D.4D";"IN:",Fo*Co,Fo*Oo,Fo*Ho
6040 PRINT USING "10A,2D.4D,3X,2D.4D,3X,2D.4D";"OUT:",Fpm*Cp+Fmm*Cme,Fpm*Op+Fmm*
Ome,Fpm*Hp+Fmm*Hme
6050 PRINT "  "
6060 PRINT "  "
6070 SUBEND
6080 !
6090 SUB Prt reformer
6100 Prt reformer:!
6110   COM /Tp/ Tr1,Tr2,Pr,Tm1,Tm2,Pm
6120   COM /Equilk/ Kgamref,K1r,K2r,F1r,F2r,Kgamshift,Kgam6,Kgam8,K1m,K2m,F1m,F2
m
6130   COM /Composition/ Yinr(*),Yfr(*),Yinco(*),Yfco(*),Yinacid(*),Yfacid(*),Yi
nm(*),Yfm(*),Yrm(*),Ymm(*)
6140   COM /Conversion/ Xref,Yref,Xmeth,Ymeth
6150   COM /Flows/ Finr,Ffr,Finco,Ffco,Finacid,Ffacid,Finm,Ffm,Frm,Fmm,Fpm
6150   COM /Gasifier/ Fwood,Fsteam,Fchar,Fo2,Fh2o,Fcond,Fgas,Ygas(*),Fgasifier,Y
gasifier(*),Twood,Tsteam,Tgas,To2,Char yield,Ext ht supply,Gasifier$
```

```
6170   COM /Reformer/ Steam.Methane.Yoasin(*).Foasin.Ua.Ref stack o2
6180   COM /Element/ Co.Cp.Cme.Oo.Op.Ome.Ho.Hp.Hme
6190   COM /Temperatura/ T(*)
6200   COM /Combustion/ Fcombgas.Stack o2
6210   PRINT "REFORMER"
6220 PRINT USING "2X.8A.4D.4D";"TEMP.'C=".Tr1
6230 PRINT USING "2X.11A.4D.4D";"PRESS. ATM=".Pr
6240 PRINT USING "2X.15A.4D.4D";"K1 (REFORMING)=".K1r
6250 PRINT USING "2X.11A.2D.4D";"K2 (SHIFT)=".K2r
6260 PRINT USING "2X.2A.2D.4D.2X.4A.2D.4D.1A";"X=".Xref."(K2=".F2r+K2r.")"
6270 PRINT USING "2X.2A.2D.4D.2X.4A.4D.4D.1A";"Y=".Yref."(K1=".F1r+K1r.")"
6280 PRINT USING "18X.4A.8X.4A.8X.5A";"Yoasin"."Yinr"."Youtr"
6290 PRINT USING "15A.2D.5D.4X.2D.5D.4X.2D.5D";"CO:".Yoasin(1).Yinr(1).Yfr(1)
6300 PRINT USING "15A.2D.5D.4X.2D.5D.4X.2D.5D";"CO2:".Yoasin(2).Yinr(2).Yfr(2)
6310 PRINT USING "15A.2D.5D.4X.2D.5D.4X.2D.5D";"CH3OH:".Yoasin(5).Yinr(3).Yfr(3)
6320 PRINT USING "15A.2D.5D.4X.2D.5D.4X.2D.5D";"H2:".Yoasin(4).Yinr(4).Yfr(4)
6330 PRINT USING "15A.2D.5D.4X.2D.5D.4X.2D.5D";"H2O:".Yoasin(5).Yinr(5).Yfr(5)
6340 PRINT USING "15A.2D.5D.4X.2D.5D.4X.2D.5D";"CH4:".Yoasin(6).Yinr(6).Yfr(6)
6350 PRINT USING "15A.2D.5D.4X.2D.5D.4X.2D.5D";"N2:".Yoasin(7).Yinr(7).Yfr(7)
6360 PRINT USING "15A.2D.5D.4X.2D.5D.4X.2D.5D";"FLOW RATE. M/t=".Foasin.Finr.Ffr
6370 PRINT USING "15X.6A.2D.5D";"STEAM=".Steam
6380 PRINT "  "
6390 PRINT "CHECK ELEMENT BALANCE:"
6400 PRINT USING "14X.9A.9A.9A";"C"."O"."H"
6410 CALL Elementbal(Yoasin(*).Yfr(*).Yoas(*))
6420 PRINT USING "10A.2D.4D.2X.2D.4D.2X.2D.4D";"IN:".Co*Foasin.Oo*Foasin+Steam.H
o*Foasin+2*Steam
6430 PRINT USING "10A.2D.4D.2X.2D.4D.2X.2D.4D";"OUT:".Cp*Ffr.Op*Ffr.Hp*Ffr
6440 PRINT "  "
6450 PRINT "EXCHANGER DESIGN"
6460 PRINT USING "2X.3A.3D.1D";"UA=".Ua
6470 PRINT USING "10X.5A.5X.6A";"INLET"."OUTLET"
6480 PRINT USING "2X.8A.3D.1D.6X.3D.1D";"HOT:".Tr1.T(2)
6490 PRINT USING "2X.8A.3D.1D.6X.3D.1D";"COLD:".T(1).T(3)
6500 PRINT "COMBUSTION:"
6510 PRINT USING "2X.20A";"SYNGAS USED FOR FUEL"
6520 PRINT USING "2X.12A.2D.D";"STACK O2. %=".Ref stack o2*100
6530 PRINT USING "2X.10A.2D.4D";"FLOW. M/t=".Fcombgas
6540 PRINT "  "
6550 PRINT "GASIFIER SYNGAS FLOW. M/T=";Fcombgas+Fgas
6560 PRINT "  "
6570 PRINT "  "
6580 PRINT "  "
6590 SUBEND
6600 !
6610 SUB Stream mix(Yo(*).Fo.Y1(*).F1.Y2(*).F2)
6620 !THIS SUB MIXES TWO STREAMS "O" AND "1" AND DETERMINES THE FLOW AND
COMPOSITION OF THE NEW STREAM
6630 Stream mix:!
6640  INTEGER I
6650  F2=Fo+F1
```

```
6660  FOR I=1 TO 7
6670  Y2(I)=(Yo(I)*Fo+Y1(I)*F1)/F2
6680  NEXT I
6690  SUBEND
6700  !
6710  SUB Yfmeoh co(X,Y,Yin(*),Fin,Yf(*),Fout)
6720  !DETERMINE THE COMPOSITION AND THE FLOW OF THE OUTLET OF THE METHANOL SYNT
HESIS REACTOR AND CO SHIFT REACTOR GIVEN X,Y,YIN AND FIN
6730 Yfmeoh co: !
6740  Den=1-2*X
6750  Yf(1)=(Yin(1)-X+Y)/Den
6760  Yf(2)=(Yin(2)-Y)/Den
6770  Yf(3)=(Yin(3)+X)/Den
6780  Yf(4)=(Yin(4)-2*X-Y)/Den
6790  Yf(5)=(Yin(5)+Y)/Den
6800  Yf(6)=Yin(6)/Den
6810  Yf(7)=Yin(7)/Den
6820  Fout=Den*Fin
6830  SUBEND
6840  !
6850  SUB Co shift
6860 Co shift: !
6870   COM /Composition/ Yinr(*),Yfr(*),Yinco(*),Yfco(*),Yinacid(*),Yfacid(*),Yi
nm(*),Yfm(*),Yrm(*),Ymm(*)
6880   COM /Flows/ Finr,Ffr,Finco,Ffco,Finacid,Ffacid,Finm,Ffm,Frm,Fmm,Fpm
6890   COM /Gasifier/ Fwood,Fsteam,Fchar,Fo2,Fh2o,Fcond,Fgas,Ygas(*),Fgasifier,Y
gasifier(*),Twood,Tsteam,Tgas,To2,Char yield,Ext ht supply,Gasifier$
6900   COM /Co shift/ Tco,Pco,Kgamco,Fbyco,Youtco(*),Foutco,Fco steam
6910   COM Ytemp(*)
6920   Fco steam=0
6930   !CHECK IF SHIFT IS REQUIRED
6940   FOR I=1 TO 8
6950   Yinacid(I)=Yfr(I)
6960   Yfco(I)=Yfr(I)
6970   Yinco(I)=0
6980   Youtco(I)=0
6990   NEXT I
7000   Ffco=Ffr
7010   Finacid=Ffr
7020   Fbyco=Ffr
7030   Finco=0
7040   Foutco=0
7050   CALL Acid rem(Yinacid(*),Finacid,Yfacid(*),Ffacid)
7060   F1=(Yfacid(4)-Yfacid(2))/(Yfacid(1)+Yfacid(2))-2.1
7070   !IF F1>0 THEN NO CO SHIFT REQUIRED
7080   IF (F1>0) THEN GOTO Finish1
7090   !DETERMINE BALANCE RATIO IF ALL OF REFORMER OUTLET IS SHIFTED
7100   FOR I=1 TO 8
7110   Yinco(I)=Yfr(I)
7120   NEXT I
7130   Finco=Ffr
```

```
7140   Fbyco=0
7150   T=Tco+273
7160   CALL Kshift(T,K2)
7170   X=0
7180   K2=K2/Kgamco
7190   CALL Recursion(Yinco(*),X,Y,K2)
7200   Fbyco=0
7210   Finco=Ffr-Fbyco
7220   CALL Yfmeoh co(X,Y,Yinco(*),Finco,Youtco(*),Foutco)
7230   CALL Stream mix(Youtco(*),Foutco,Yinco(*),Fbyco,Yinacid(*),Finacid)
7240   CALL Acid rem(Yinacid(*),Finacid,Yfacid(*),Ffacid)
7250   F1=(Yfacid(4)-Yfacid(2))/(Yfacid(1)+Yfacid(2))-2.1
7260   IF (F1<0) THEN GOTO Steam addition
7270   X1=Fbyco
7280 Detbal:  !
7290   Xn=X1+.001/Ffr
7300   Finco=Ffr-Xn
7310   Foutco=Finco
7320   CALL Stream mix(Youtco(*),Foutco,Yinco(*),Xn,Yinacid(*),Finacid)
7330   CALL Acid rem(Yinacid(*),Finacid,Yfacid(*),Ffacid)
7340   Fn=(Yfacid(4)-Yfacid(2))/(Yfacid(1)+Yfacid(2))-2.1
7350   CALL Newton raphson(X1,F1,Xn,Fn,Xnew)
7360   Finco=Ffr-Xnew
7370   Foutco=Finco
7380   CALL Stream mix(Youtco(*),Foutco,Yinco(*),Xnew,Yfco(*),Ffco)
7390   CALL Acid rem(Yfco(*),Ffco,Yfacid(*),Ffacid)
7400   Few=(Yfacid(4)-Yfacid(2))/(Yfacid(1)+Yfacid(2))-2.1
7410   IF (ABS(Few)<2.1/200) THEN GOTO Finish
7420   X1=Xnew
7430   F1=Few
7440   GOTO Detbal
7450 Finish:  !
7460           Fbyco=Xnew
7470           FOR I=1 TO 7
7480           Yinacid(I)=Yfco(I)
7490           NEXT I
7500           Finacid=Ffco
7510   GOTO Finish1
7520 Steam addition:  !
7530   !DETERMINE STEAM ADDITION TO INLET GAS OF CO SHIFT
7540   X1=0
7550   X1new=.001*Yinco(1)
7560 Repeat steam:  !
7570   !DETERMINE NEW INLET COMPOSTION
7580   Ftemp=Finco+X1new
7590   FOR I=1 TO 8
7600   Ytemp(I)=Yinco(I)*Finco/Ftemp
7610   NEXT I
7620   Ytemp(5)=(Yinco(5)*Finco+X1new)/Ftemp
7630   CALL Recursion(Ytemp(*),X,Y,K2)
7640   CALL Yfmeoh co(X,Y,Ytemp(*),Ftemp,Youtco(*),Foutco)
7650   FOR I=1 TO 8
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```
7660   Yinacid(I)=Youtco(I)
7670   Yfco(I)=Youtco(I)
7680   NEXT I
7690   Finacid=Foutco
7700   Ffco=Foutco
7710   CALL Acid rem(Yinacid(*).Finacid.Yfacid(*).Ffacid)
7720   F1new=(Yfacid(4)-Yfacid(2))/(Yfacid(1)+Yfacid(2))-2.1
7730   IF (ABS(F1new)<2.1/200) THEN GOTO Finish2
7740   CALL Newton raphson(X1.F1.X1new.F1new.Xnew)
7750   X1=X1new
7760   F1=F1new
7770   X1new=Xnew
7780   GOTO Repeat steam
7790 Finish2:  !
7800   FOR I=1 TO 8
7810   Yinco(I)=Ytemp(I)
7820   NEXT I
7830   Finco=Ftemp
7840   Fco steam=X1new
7850 Finish1:  !
7860   SUBEND
7870   !
7880   SUB Prt co shift
7890 Prt co shift:  !
7900   COM /Composition/ Yinr(*).Yfr(*).Yinco(*).Yfco(*).Yinacid(*).Yfacid(*).Yi
nm(*).Yfm(*).Yrm(*).Ymm(*)
7910   COM /Flows/ Finr.Ffr.Finco.Ffco.Finacid.Ffacid.Finm.Ffm.Frm.Fmm.Fom
7920   COM /Gasifier/ Fwood.Fsteam.Fchar.Fo2.Fh2o.Fcond.Fgas.Ygas(*).Fgasifier.Y
gasifier(*).Twood.Tsteam.Tgas.To2.Char yield.Ext ht supply.Gasifier$
7930   COM /Co shift/ Tco.Pco.Kgamco.Fbyco.Youtco(*).Foutco.Fco steam
7940   PRINT "CO SHIFT"
7950   PRINT USING "9A.4D";"TEMP .°C=".Tco
7960   PRINT USING "11A.3D.D";"PRESS. ATM=".Pco
7970   PRINT USING "20A.3D.3D";"STEAM ADDITION. M/t=";Fco steam
7980   PRINT USING "12X.9A.9A.9A";"Yinco"."Youtco"."Yfco"
7990   PRINT USING "10A.2D.4D.2X.2D.4D.2X.2D.4D";"CO:".Yinco(1).Youtco(1).Yfco(1
)
8000   PRINT USING "10A.2D.4D.2X.2D.4D.2X.2D.4D";"CO2:".Yinco(2).Youtco(2).Yfco(
2)
8010   PRINT USING "10A.2D.4D.2X.2D.4D.2X.2D.4D";"CH3OH:".Yinco(3).Youtco(3).Yfc
o(3)
8020   PRINT USING "10A.2D.4D.2X.2D.4D.2X.2D.4D";"H2:".Yinco(4).Youtco(4).Yfco(4
)
8030   PRINT USING "10A.2D.4D.2X.2D.4D.2X.2D.4D";"H2O:".Yinco(5).Youtco(5).Yfco(
5)
8040   PRINT USING "10A.2D.4D.2X.2D.4D.2X.2D.4D";"CH4:".Yinco(6).Youtco(6).Yfco(
6)
8050   PRINT USING "10A.2D.4D.2X.2D.4D.2X.2D.4D";"N2:".Yinco(7).Youtco(7).Yfco(7
)
8060   PRINT USING "10A.2D.4D.2X.2D.4D.2X.2D.4D";"FLOW. M/t:".Finco.Foutco.Ffco
8070   PRINT USING "10X.7A.2D.4D";"BYPASS:";Fbyco
```

```
8080   PRINT " "
8090   PRINT " "
8100   PRINT " "
8110   SUBEND
8120   !
8130   SUB Acid rem(Yinacid(*),Finacid,Yfacid(*),Ffacid)
8140 Acid rem:  !
8150   COM /Acid rem/ Yfco2,Yfh2o,Tacid rem
8160   INTEGER I
8170   Yfacid(2)=Yfco2
8180   Yfacid(5)=Yfh2o
8190   F=0
8200   FOR I=1 TO 8
8210   IF (I=2) THEN GOTO Bypass
8220   IF (I=5) THEN GOTO Bypass
8230   F=F+Yinacid(I)*Finacid
8240 Bypass:  !
8250   NEXT I
8260   Ffacid=F/(1-Yfacid(2)-Yfacid(5))
8270   FOR I=1 TO 8
8280   IF (I=2) THEN GOTO Bypass1
8290   IF (I=5) THEN GOTO Bypass1
8300   Yfacid(I)=Yinacid(I)*Finacid/Ffacid
8310 Bypass1:  !
8320   NEXT I
8330   SUBEND
8340   !
8350   SUB Prt acid rem
8360 Prt acid rem:  !
8370   COM /Composition/ Yinr(*),Yfr(*),Yinco(*),Yfco(*),Yinacid(*),Yfacid(*),Yi
nm(*),Yfm(*),Yrm(*),Ymm(*)
8380   COM /Flows/ Finr,Ffr,Finco,Ffco,Finacid,Ffacid,Finm,Ffm,Frm,Fmm,Fpm
8390   COM /Gasifier/ Fwood,Fsteam,Fchar,Fo2,Fh2o,Fcond,Fgas,Ygas(*),Fgasifier,Y
gasifier(*),Twood,Tsteam,Tgas,To2,Char yield,Ext ht supply,Gasifier$
8400   COM /Acid rem/ Yfco2,Yfh2o,Tacid rem
8410   PRINT "ACID GAS REMOVAL"
8420   PRINT USING "2X,5A,3D.2D,3A";"TEMP:",Tacid gas," C"
8430   PRINT USING "12X,9A,9A";"YINACID","YOUTACID"
8440   PRINT USING "10A,2D.4D,2X,2D.4D";"CO:",Yinacid(1),Yfacid(1)
8450   PRINT USING "10A,2D.4D,2X,2D.4D";"CO2:",Yinacid(2),Yfacid(2)
8460   PRINT USING "10A,2D.4D,2X,2D.4D";"CH3OH:",Yinacid(3),Yfacid(3)
8470   PRINT USING "10A,2D.4D,2X,2D.4D";"H2:",Yinacid(4),Yfacid(4)
8480   PRINT USING "10A,2D.4D,2X,2D.4D";"H2O:",Yinacid(5),Yfacid(5)
8490   PRINT USING "10A,2D.4D,2X,2D.4D";"CH4:",Yinacid(6),Yfacid(6)
8500   PRINT USING "10A,2D.4D,2X,2D.4D";"N2:",Yinacid(7),Yfacid(7)
8510   PRINT USING "10A,2D.4D,2X,2D.4D";"FLOWS,M/t:",Finacid,Ffacid
8520   PRINT USING "10A,2D.4D";"BAL RATIO=",(Yfacid(4)-Yfacid(2))/(Yfacid(1)+Yfa
cid(2))
8530   PRINT " "
8540   PRINT " "
8550   PRINT " "
```

```
8560   SUBEND
8570   !
8580   SUB Newton raphson(X1,F1,X2,F2,Xnew)
8590 Newton raphson:  !
8600   !DETERMINE DERIVATIVE
8610   Derivf=(F2-F1)/(X2-X1)
8620   !DETERMINE NEW VALUE OF X
8630   Xnew=X2-F2/Derivf
8640   SUBEND
8650   !
8660   SUB Reformer(Yo(*),Fo)
8670   !DETERMINE STEAM INPUT AND EXIT COMPOSITION GIVEN INPUT SYNGAS FLOW AND C
OMPOSTION
8680 Reformer:  !
8690   COM /Composition/ Yinr(*),Yfr(*),Yinco(*),Yfco(*),Yinacid(*),Yfacid(*),Yi
nm(*),Yfm(*),Yrm(*),Ymm(*)
8700   COM /Flows/ Finr,Ffr,Finco,Ffco,Finacid,Ffacid,Finm,Ffm,Frm,Fmm,Fpm
8710   COM /Gasifier/ Fwood,Fsteam,Fchar,Fo2,Fh2o,Fcond,Fgas,Ygas(*),Fgasifier,Y
gasifier(*),Twood,Tsteam,Tgas,To2,Char yield,Ext ht supply,Gasifier$
8720   COM /Reformer/ Steam Methane,Ygasin(*),Fgasin,Ua,Ref stack o2
8730   INTEGER I
8740   Steam=0
8750   CALL Equilibriumr(Yo(*),Fo)
8760   IF (ABS(Methane-Yfr(6))<Methane/10) THEN GOTO Finish2
8770   IF (Yfr(6)<Methane) THEN GOTO Finish2
8780   Steam1=1.005*((Yo(6)-Methane)/(1+2*Methane)-Yo(5))*Fo
8790   IF (Steam1<0) THEN GOTO Steamby
8800   Steam=Steam1
8810   CALL Refmix(Yo(*),Fo,Steam,Yinr(*),Finr)
8820   CALL Equilibriumr(Yinr(*),Finr)
8830   IF (Yfr(6)<Methane) THEN GOTO Finish
8840   IF (ABS(Methane-Yfr(6))<Methane/10) THEN GOTO Finish
8850 Steamby:  !
8860   X1=Steam
8870   F1=Yfr(6)-Methane
8880 Detsteam:  !
8890   Xn=X1+.05*Fo
8900   CALL Refmix(Yo(*),Fo,Xn,Yinr(*),Finr)
8910   CALL Equilibriumr(Yinr(*),Finr)
8920   Steam=Xn
8930   Fn=Yfr(6)-Methane
8940   CALL Newton raphson(X1,F1,Xn,Fn,Xnew)
8950   CALL Refmix(Yo(*),Fo,Xnew,Yinr(*),Finr)
8960   CALL Equilibriumr(Yinr(*),Finr)
8970   IF (ABS(Methane-Yfr(6))<Methane/10) THEN GOTO Finish
8980   IF (Yfr(6)<Methane) THEN GOTO Finish
8990   X1=Xnew
9000   F1=Yinr(6)-Methane
9010   GOTO Detsteam
9020 Finish2:  !
9030   FOR I=1 TO 6
```

```
9040   Yinr(I)=Yo(I)
9050   NEXT I
9060   Finr=Fo
9070   GOTO Finish1
9080 Finish:  !
9090   Steam=Xnew
9100 Finish1:  !
9110   SUBEND
9120   !
9130   SUB Refmix(Yo(*),Fo,Xn,Yinr(*),Finr)
9140   !SIMPLE MIX FOR SYNGAS TO REFORMER AND STEAM
9150 Refmix:  !
9160   INTEGER I
9170   FOR I=1 TO 8
9180   Yinr(I)=Yo(I)*Fo/(Fo+Xn)
9190   NEXT I
9200   Yinr(5)=(Yo(5)*Fo+Xn)/(Fo+Xn)
9210   Finr=Fo+Xn
9220   SUBEND
9230   !
9240   SUB Prt syngas(Ygas(*),Fgas)
9250   !PRINT INITIAL CONDITIONS
9260 Prt syngas:  !
9270   PRINT "SYNTHESIS GAS:"
9280   PRINT USING "10A,2D.4D";"CO:",Ygas(1)
9290   PRINT USING "10A,2D.4D";"CO2:",Ygas(2)
9300   PRINT USING "10A,2D.4D";"CH3OH:",Ygas(3)
9310   PRINT USING "10A,2D.4D";"H2:",Ygas(4)
9320   PRINT USING "10A,2D.4D";"H2O:",Ygas(5)
9330   PRINT USING "10A,2D.4D";"CH4:",Ygas(6)
9340   PRINT USING "10A,2D.4D";"N2:",Ygas(7)
9350   PRINT USING "10A,2D.4D";"FLOW, M/t:",Fgas
9360   PRINT "  "
9370   PRINT "  "
9380   PRINT "  "
9390   SUBEND
9400   !
9410   SUB Sign(F,Test$)
9420   !DETERMINE IF F IS POSITIVE OR NEGATIVE
9430 Sign:  !
9440   IF (F<0) THEN GOTO Test
9450   Test$="B"
9460   GOTO Tskip
9470 Test:  !
9480   Test$="A"
9490 Tskip:  !
9500   SUBEND
9510   !
9520   SUB Process logic
9530 Process logic: !
9540   COM /Tp/ Tr1,Tr2,Pr,Tm1,Tm2,Pm
```

```
9550   COM /Equilk/ Kgamref.K1r.K2r.F1r.F2r.Kgamshift.Kgam6.Kgam8.K1m.K2m.F1m.F2
m
9560   COM /Composition/ Yinr(*).Yfr(*).Yinco(*).Yfco(*).Yinacid(*).Yfacid(*).Yi
nm(*).Yfm(*).Yrm(*).Ymm(*)
9570   COM /Conversion/ Xref.Yref.Xmeth.Ymeth
9580   COM /Flows/ Finr.Ffr.Finco.Ffco.Finacid.Ffacid.Finm.Ffm.Frm.Fmm.Fpm
9590   COM /Gasifier/ Fwood.Fsteam.Fchar.Fo2.Fh2o.Fcond.Fgas.Ygas(*).Fgasifier.Y
gasifier(*).Twood.Tsteam.Tgas.To2.Char yield.Ext ht supply.Gasifier$
9600   COM /Co shift/ Tco.Pco.Kgamco.Fbyco.Youtco(*).Foutco.Fco steam
9610   COM /Reformer/ Steam.Methane.Ygasin(*).Fgasin.Ua.Ref stack o2
9620   COM /Acid rem/ Yfco2.Yfh2o.Tacid gas
9630   COM /Combustion/ Fcombgas.Stack o2
9640   COM /Compression/ Hcomp(*)
9650   COM /Oxygen/ Power
9660   COM /Boiler/ Fboiler wood.Tlower steam.Thigher steam.Boiler stack o2.Turb
ine eff.Avail ht.Mc char.Fsteam boiler
9670   COM /Wood/ Wood(*).Subc.Subh.Subo.Mwood.Hfwood
9680   COM /Efficiency/ C conv.First law
9690   COM /Dryer/ Ffdry wood.Fdryer wood.Tdryer.Dryer stack o2.Fevap
9700   COM /Capital2/ Boiler.Misc offsite.Blcc.Offsite.Plant
9710   COM /Operating/ Wood cost.Tot mat util.Tot labour.Capital.Total operating
9720   COM /Target meth/ Target
9730   COM /Price/ Supply price.Interest.Years
9740   INTEGER I.Ii.J.Kk
9750   !***********
9760  !GOTO Finish
9770   !***********
9780   !*****************************
9790   !CHECK THAT GAS COMPOSITION IS CONSISTENT WITH MASS BALANCE ON GASIFIER
9800  CALL Gasifier(Ygas(*).Fgas+Fcombgas.Char yield.Tsteam.Tgas.Fwood.Fsteam.Fc
har.Fo2.Fh2o.Fcond.Fgasifier.Ygasifier(*).Ext ht supply.Gasifier$)
9810  IF (Fo2<0) THEN GOTO Gas error
9820  GOTO Gas okay
9830 Gas error: !
9840  PRINT "GAS COMPOSITION IS NOT CONSISTENT WITH GASIFIER MASS & HEAT BAL"
9850  CALL Prt gasifier
9860  STOP
9870 Gas okay: !
9880  !RECYCLE PURGE TO INLET OF REFORMER
9890  !CHECK CONVERGENCE USING PURGECONV
9900  Fpm=0
9910  Purgeconv=Fpm*Yrm(6)
9920 Iterateagain: !
9930                 PRINT "PURGECONV=";Purgeconv
9940  CALL Stream mix(Ygas(*).Fgas.Yrm(*).Fpm.Ygasin(*).Fgasin)
9950  CALL Reformer(Ygasin(*).Fgasin)
9960  CALL Co shift
9970  CALL Methanol(Yfacid(*).Ffacid)
9980  IF (ABS(Purgeconv-Fpm*Yrm(6))<Purgeconv/100) THEN GOTO Finish
9990  Purgeconv=Fpm*Yrm(6)
10000 GOTO Iterateagain
```

```
10010 Finish:!
10020      !****************
10030    ! CALL Data retrieve
10040      !****************
10050        CALL Ht bal ref
10060 CALL Gasifier(Ygas(*).Fgas+Fcombgas.Char yield.Tsteam.Tgas.Fwood.Fsteam.Fc
har.Fo2.Fh2o.Fcond.Fgasifier.Ygasifier(*).Ext ht supply.Gasifier$)
10070 CALL Dryer
10080        Hcomp(1.2)=Tacid gas
10090        Hcomp(1.4)=Pco
10100        Hcomp(1.5)=Pm/101.325
10110        Hcomp(2.2)=Tm1
10120 !RECYCLE COMPRESSION: ASSUME DEL P ACROSS REACTOR IS 30PSI(205kPa)
10130        Hcomp(2.4)=(Pm-205)/101.325
10140        Hcomp(2.5)=Hcomp(1.5)
10150 CALL Compressor(Yfacid(*).Ffacid.Tacid gas+273.Hcomp(1.3).Pco.Hcomp(1.5).H
comp(1.1))
10160 CALL Compressor(Yrm(*).Frm,Tm1+273.Hcomp(2.3).Hcomp(2.4).Hcomp(2.5).Hcomp(
2.1))
10170 Hcomp(1.3)=Hcomp(1.3)-273
10180 Hcomp(2.3)=Hcomp(2.3)-273
10190 CALL Oxygen(Fo2.Power)
10200 Tl=Tlower steam
10210 Th=Thigher steam
10220 Mc char=50
10230 !ASSUME NON-CONDENSING TURBINE IN BOILER CIRCUIT
10240 !GENERATED POWER MUST BE SUFFICIENT FOR COMPRESSION AND GASIFIER EXT HEAT
10250 !GASIFIER EXT HT IS SUPPLIED ELECTRICALLY WITH GENERATOR EFF OF 0.95
10260 IF (Ext ht supply<0) THEN GOTO Logicby
10270 Gen power=Hcomp(1.1)+Hcomp(2.1)+Power+Ext ht supply/.95
10280 GOTO Logicby1
10290 Logicby:!
10300 Gen power=Hcomp(1.1)+Hcomp(2.1)+Power
10310 Logicby1:!
10320 Ext ht=Ext ht supply
10330  CALL Boiler(Fboiler wood.Mwood.Wood(8).Fchar.Mc char.Subc.Subh.Subo.Tl.Th
.Gen power.Turbine eff.Boiler stack o2.Hfwood.Avail ht.Fstbl.Ext ht.Fsteam)
10340  Fsteam boiler=Fstbl
10350  CALL Efficiency(Ymm(I).Fmm.Fdryer wood.Fboiler wood.Subc.Mwood.Wood(7).(W
ood(4)+Wood(5))/100.C conv.First law)
10360  Mw=Mwood
10370  Targ=Target
10380  Fdry w=Fdryer wood
10390  Yrgas=Ygasin(6)
10400  Yr=Yfr(6)
10410  Yco=Yinco(1)
10420  Yoco=Youtco(1)
10430  Yacid=Yinacid(2)
10440  Yfa=Yfacid(2)
10450  Yme=Ymm(1)
10460  Foco=Foutco
```

```
10470  Total power=Hcomp(1,1)+Hcomp(2,1)+Power
10480  CALL Plant capital(Mw,Targ,Fdry w,Fwood,Fgasin,Yrgas,Ffr,Yr,Finco,Yco,Foc
o,Yoco,Finacid,Yacid,Ffacid,Yfa,Fmm,Yme,Fo2,Total power,Fsteam boiler,Gasifier$)
10490  CALL Operat maint(Fdryer wood,Fboiler wood,Mwood,Target,Fmm,Yme,Gasifier$
)
10500  CALL Supply price(Plant,Total operating,Target)
10510  !***************
10520 !CALL Data store
10530  !***************
10540  CALL Process print
10550 BEEP
10560 BEEP
10570 BEEP
10580 SUBEND
10590 !
10600 SUB Data store
10610 !STORE MASS BAL DATA IN SERIAL ACCESS FILE
10620 Data store:!
10630  COM /Tp/ Tr1,Tr2,Pr,Tm1,Tm2,Pm
10640  COM /Equilk/ Kgamref,K1r,K2r,F1r,F2r,Kgamshift,Kgam6,Kgam8,K1m,K2m,F1m,F2
m
10650  COM /Composition/ Yinr(*),Yfr(*),Yinco(*),Yfco(*),Yinacid(*),Yfacid(*),Yi
nm(*),Yfm(*),Yrm(*),Ymm(*)
10660  COM /Conversion/ Xref,Yref,Xmeth,Ymeth
10670  COM /Flows/ Finr,Ffr,Finco,Ffco,Finacid,Ffacid,Finm,Ffm,Frm,Fmm,Fpm
10680  COM /Gasifier/ Fwood,Fsteam,Fchar,Fo2,Fh2o,Fcond,Fgas,Ygas(*),Fgasifier,Y
gasifier(*),Twood,Tsteam,Tgas,To2,Char yield,Ext ht supply,Gasifier$
10690  COM /Reformer/ Steam,Methane,Ygasin(*),Fgasin,Ua,Ref stack o2
10700  COM /Co shift/ Tco,Pco,Kgamco,Fbyco,Youtco(*),Foutco,Fco steam
10710  COM /Data storage/ A(*)
10720  COM /Methanol/ Frstore,Yr target,Indicator$[8]
10730  COM /Temperature/ T(*)
10740  COM /Combustion/ Fcombgas,Stack o2
10750  COM /Wood/ Wood(*),Subc,Subh,Subo,Mwood,Hfwood
10760  COM /Dryer/ Ffdry wood,Fdryer wood,Tdryer,Dryer stack o2,Fevap
10770  COM /Boiler/ Fboiler wood,Tlower steam,Thigher steam,Boiler stack o2,Turb
ine eff,Avail ht,Mc char,Fsteam boiler
10780  INTEGER I
10790  BEEP
10800  BEEP
10810  INPUT "NAME OF DATA FILE=",Name$
10820  PRINT "DATA FILE:";Name$
10830  PRINT "  "
10840  PRINT "  "
10850  CREATE BDAT Name$,1,1224
10860  !PUT DATA INTO AN ARRAY FOR STORING
10870  FOR I=1 TO 7
10880  A(1,I)=Ygas(I)
10890  A(2,I)=Ygasin(I)
10900  A(3,I)=Yinr(I)
10910  A(4,I)=Yfr(I)
```

```
10920  A(5,I)=Yinco(I)
10930  A(6,I)=Youtco(I)
10940  A(7,I)=Yfco(I)
10950  A(8,I)=Yinacid(I)
10960  A(9,I)=Yfacid(I)
10970  A(10,I)=Yinm(I)
10980  A(11,I)=Yfm(I)
10990  A(12,I)=Yrm(I)
11000  NEXT I
11010  A(13,1)=Ymm(1)
11020  A(13,2)=Ymm(2)
11030  A(13,3)=Tgas
11040  A(13,4)=Char yield
11050  A(13,5)=Tsteam
11060  A(13,6)=T(1)
11070  A(13,7)=Mathane
11080  A(1,8)=Fgas
11090  A(2,8)=Fgasin
11100  A(3,8)=Finr
11110  A(4,8)=Ffr
11120  A(5,8)=Finco
11130  A(6,8)=Foutco
11140  A(7,8)=Ffco
11150  A(8,8)=Finacid
11160  A(9,8)=Ffacid
11170  A(10,8)=Finm
11180  A(11,8)=Ffm
11190  A(12,8)=Frm
11200  A(13,8)=Fmm
11210  A(14,1)=Steam
11220  A(14,2)=Fbyco
11230  A(14,3)=Fom
11240  A(14,4)=Xref
11250  A(14,5)=Yref
11260  A(14,6)=Xmeth
11270  A(14,7)=Ymeth
11280  A(14,8)=Tr1
11290  A(15,1)=Tco
11300  A(15,2)=Tm1
11310  A(15,3)=Pr
11320  A(15,4)=Pco
11330  A(15,5)=Pm
11340  A(15,6)=K1r
11350  A(15,7)=K2r
11360  A(15,8)=F1r
11370  A(16,1)=F2r
11380  A(16,2)=K1m
11390  A(16,3)=K2m
11400  A(16,4)=F1m
11410  A(16,5)=F2m
11420  A(16,6)=Fco steam
```

```
11430  FOR I=1 TO 8
11440  A(17,I)=Wood(I)
11450  NEXT I
11460  A(18,1)=Tdryer
11470  A(18,2)=Dryer stack o2
11480  A(18,3)=Tlower steam
11490  A(18,4)=Thigher steam
11500  A(18,5)=Boiler stack o2
11510  A(18,6)=Turbine eff
11520  A(18,7)=Tacid gas
11530  A(18,8)=Yfco2
11540  A(19,1)=Yfh2o
11550  A(19,2)=Ref stack o2
11560  A(19,3)=Frstore
11570  ASSIGN @Path1 TO Name$
11580  OUTPUT @Path1,1;A(*)
11590  ASSIGN @Path1 TO *
11600 Finish: !
11610  SUBEND
11620  !
11630  SUB Data retrieve
11640 Data retrieve: !
11650  COM /Tp/ Tr1,Tr2,Pr,Tm1,Tm2,Pm
11660  COM /Equilk/ Kgamref,K1r,K2r,F1r,F2r,Kgamshift,Kgam6,Kgam8,K1m,K2m,F1m,F2
m
11670  COM /Composition/ Yinr(*),Yfr(*),Yinco(*),Yfco(*),Yinacid(*),Yfacid(*),Yi
nm(*),Yfm(*),Yrm(*),Ymm(*)
11680  COM /Conversion/ Xref,Yref,Xmeth,Ymeth
11690  COM /Flows/ Finr,Ffr,Finco,Ffco,Finacid,Ffacid,Finm,Ffm,Frm,Fmm,Fpm
11700  COM /Gasifier/ Fwood,Fsteam,Fchar,Fo2,Fh2o,Fcond,Fgas,Ygas(*),Fgasifier,Y
gasifier(*),Twood,Tsteam,Tgas,To2,Char yield,Ext ht supply,Gasifier$
11710  COM /Reformer/ Steam,Methane,Ygasin(*),Fgasin,Ua,Ref stack o2
11720  COM /Co shift/ Tco,Pco,Kgamco,Fbyco,Youtco(*),Foutco,Fco steam
11730  COM /Data storage/ A(*)
11740  COM /Methanol/ Frstore,Yr target,Indicator$[8]
11750  COM /Temperature/ T(*)
11760  COM /Combustion/ Fcombgas,Stack o2
11770  COM /Dryer/ Ffdry wood,Fdryer wood,Tdryer,Dryer stack o2,Fevap
11780  COM /Wood/ Wood(*),Subc,Subh,Subo,Mwood,Hfwood
11790  COM /Boiler/ Fboiler wood,Tlower steam,Thigher steam,Boiler stack o2,Turb
ine eff,Avail ht,Mc char,Fsteam boiler
11800  INTEGER I
11810  PRINT "RETRIEVE MASS BALANCE DATA FOR INDIRECT LIQUEFACTION"
11820  BEEP
11830  INPUT "DATA FILE NAME=",Name$
11840  ASSIGN @Path1 TO Name$
11850  ENTER @Path1,1;A(*)
11860  FOR I=1 TO 7
11870  Ygas(I)=A(1,I)
11880  Ygasin(I)=A(2,I)
11890  Yinr(I)=A(3,I)
```

```
11900  Yfr(I)=A(4,I)
11910  Yinco(I)=A(5,I)
11920  Youtco(I)=A(6,I)
11930  Yfco(I)=A(7,I)
11940  Yinacid(I)=A(8,I)
11950  Yfacid(I)=A(9,I)
11960  Yinm(I)=A(10,I)
11970  Yfm(I)=A(11,I)
11980  Yrm(I)=A(12,I)
11990  NEXT I
12000  Ymm(1)=A(13,1)
12010  Ymm(2)=A(13,2)
12020  Tgas=A(13,3)
12030  Char yield=A(13,4)
12040  Tsteam=A(13,5)
12050  T(1)=A(13,6)
12060  Methane=A(13,7)
12070  Fgas=A(1,8)
12080  Fgasin=A(2,8)
12090  Finr=A(3,8)
12100  Ffr=A(4,8)
12110  Finco=A(5,8)
12120  Foutco=A(6,8)
12130  Ffco=A(7,8)
12140  Finacid=A(8,8)
12150  Ffacid=A(9,8)
12160  Finm=A(10,8)
12170  Ffm=A(11,8)
12180  Frm=A(12,8)
12190  Fmm=A(13,8)
12200  Steam=A(14,1)
12210  Fbyco=A(14,2)
12220  Fpm=A(14,3)
12230  Xref=A(14,4)
12240  Yref=A(14,5)
12250  Xmeth=A(14,6)
12260  Ymeth=A(14,7)
12270  Tr1=A(14,8)
12280  Tco=A(15,1)
12290  Tm1=A(15,2)
12300  Pr=A(15,3)
12310  Pco=A(15,4)
12320  Pm=A(15,5)
12330  K1r=A(15,6)
12340  K2r=A(15,7)
12350  F1r=A(15,8)
12360  F2r=A(16,1)
12370  K1m=A(16,2)
12380  K2m=A(16,3)
12390  F1m=A(16,4)
12400  F2m=A(16,5)
```

```
12410  Fco steam=A(16,6)
12420  FOR I=1 TO 8
12430  Wood(I)=A(17,I)
12440  NEXT I
12450  Tdryer=A(18,1)
12460  Dryer stack o2=A(18,2)
12470  Tlower steam=A(18,3)
12480  Thigher steam=A(18,4)
12490  Boiler stack o2=A(18,5)
12500  Turbine eff=A(18,6)
12510  Tacid gas=A(18,7)
12520  Yfco2=A(18,8)
12530  Yfh2o=A(19,1)
12540  Ref stack o2=A(19,2)
12550  Frstore=A(19,3)
12560  GOTO Bypass
12570 CALL Prt syngas(Ygas(*),Fgas)
12580 PAUSE
12590 CALL Prt reformer
12600 PAUSE
12610 CALL Prt co shift
12620 PAUSE
12630 CALL Prt acid rem
12640 PAUSE
12650 CALL Prtmethanol
12660 BEEP
12670 BEEP
12680 BEEP
12690 Bypass:!
12700 ASSIGN @Path1 TO *
12710 SUBEND
12720 !
12730 SUB Heat capacity(Y(*),F,T,Cp)
12740 !DETERMINE HEAT CAPACITY OF STREAM
12750 Heat capacity:!
12760  COM /Heat capacity/ Coef(*)
12770  INTEGER I,J
12780  Cp=0
12790  FOR I=1 TO 8
12800  Cpi=Coef(I,1)+Coef(I,2)*T+Coef(I,3)*T^2+Coef(I,4)*T^3
12810  Cp=Cp+Cpi*Y(I)
12820  NEXT I
12830  Cp=F*Cp
12840  SUBEND
12850  !
12860  SUB Heat exchanger(Yh(*),Fh,Yc(*),Fc,Thin,Tcin,Thout,Tcout,Au)
12870  !HEAT EXCHANGER DESIGN USING NTU METHOD
12880  !ASSUME SIMPLE COUNTER CURRENT EXCHANGER
12890  CALL Heat capacity(Yh(*),Fh,Thin,Ch)
12900  CALL Heat capacity(Yc(*),Fc,Tcin,Cc)
12910  IF (Ch>Cc) THEN GOTO Bypass
```

```
12920  Cmin=Ch
12930  Cmax=Cc
12940  GOTO Bypass1
12950 Bypass: !
12960  Cmin=Cc
12970  Cmax=Ch
12980 Bypass1: !
12990  Ntu=Au/Cmin
13000  X=EXP(-Ntu*(1-Cmin/Cmax))
13010  Epsilon=(1-X)/(1-Cmin/Cmax*X)
13020  Qmax=Cmin*(Thin-Tcin)
13030  Q=Epsilon*Qmax
13040  Thout=Thin-Q/Ch
13050  Tcout=Q/Cc+Tcin
13060  SUBEND
13070  !
13080  SUB Ht bal ref
13090 Ht bal ref: !
13100  COM /Temperature/ T(*)
13110  COM /Tp/ Tr1,Tr2,Pr,Tm1,Tm2,Pm
13120  COM /Conversion/ Xref,Yref,Xmeth,Ymeth
13130  COM /Composition/ Yinr(*),Yfr(*),Yinco(*),Yfco(*),Yinacid(*),Yfacid(*),Yi
nm(*),Yfm(*),Yrm(*),Ymm(*)
13140  COM /Flows/ Finr,Ffr,Finco,Ffco,Finacid,Ffacid,Finm,Ffm,Frm,Fmm,Fpm
13150  COM /Gasifier/ Fwood,Fsteam,Fchar,Fo2,Fh2o,Fcond,Fgas,Ygas(*),Fgasifier,Y
gasifier(*),Twood,Tsteam,Tgas,To2,Char yield,Ext ht supply,Gasifier$
13160  COM /Reformer/ Steam,Methane,Ygasin(*),Fgasin,Ua,Ref stack o2
13170  COM /Energy/ Gf(*),Hf(*),Integral(*)
13180  COM /Combustion/ Fcombgas,Stack o2
13190  INTEGER I,J
13200  !HEAT EXCHANGER DESIGN
13210  !ASSUME HEAT EXCHANGER IS AFTER STEAM ADDITION
13220  !STEAM TEMP IS SAME AS SYNGAS TEMP
13230  !T(1):COLD STREAM INLET TEMP, 'C'
13240  !T(2):HOT STREAM OUTLET TEMP, 'C'
13250  !T(3):COLD STREAM OUTLET TEMP, 'C
13260  !UA:OVERALL HEAT TRANSFER COEFF * AREA  NORMALIZED WITHRESPECT TO FGAS
13270  Ua=100*Fgas
13280  Thin=Tr1+273
13290  Tcin=T(1)+273
13300  CALL Heat exchanger(Yfr(*),Ffr,Ygasin(*),Fgasin,Thin,Tcin,T(2),T(3),Ua)
13310  T(2)=T(2)-273
13320  T(3)=T(3)-273
13330  IF (T(2)>Tco) THEN GOTO Reaction
13340  !*****INSERT CONDITION FOR Thout<Tco
13350  PRINT "HT EX IS OVERSIZED"
13360  STOP
13370 Reaction:!
13380  !DETERMINE HEAT OF REACTION AT TR1
13390  Delhinit1=Hf(1)+3*Hf(4)-Hf(5)-Hf(6)
13400  Tref=298
```

```
13410  CALL Integral cp(Tref,Tr1+273)
13420  Sum1=Integral(1)+3*Integral(4)-Integral(5)-Integral(6)
13430  Delh1=Delhinit1+Sum1
13440  Delhinit2=Hf(1)+Hf(5)-Hf(2)-Hf(4)
13450  Sum2=Integral(1)+Integral(5)-Integral(2)-Integral(4)
13460  Delh2=Delhinit2+Sum2
13470  Htreaction=(Delh1*Xref+Delh2*Yref)*Finr
13480  !DETERMINE HEAT INPUT TO INCREASE INPUT STREAM TEMP TO REFORMING TEMP
13490  CALL Heat content(Yinr(*),Finr,T(3)+273,Tr1+273,Hstream)
13500  !DETERMINE HEAT INPUT REQUIREMENTS FOR REFORMING
13510  Heat reform=Htreaction+Hstream
13520  !DETERMINE AVAILABLE HEAT FROM COMBUSTION OF SYNGAS STREAM
13530  CALL Gas combustion(Ygas(*),1.0,T(1),Tr1,Ref stack o2,Avail ht)
13540  !DETERMINE QUANTITY OF SYNGAS WHICH IS REQUIRED TO PROVIDE HEAT FOR REFOR
MING
13550  Fcombgas=Heat reform/Avail ht
13560  SUBEND
13570  !
13580  SUB Heat content(Y(*),F,T1,T2,Delh)
13590 Heat content: !
13600  !DELH=HEAT CONTENT OF STREAM AT T2, REFERENCE TEMP=T1, 'K
13610  COM /Heat capacity/ Coef(*)
13620  COM /Energy/ Gf(*),Hf(*),Integral(*)
13630  Delh=0
13640  CALL Integral cp(T1,T2)
13650  FOR I=1 TO 8
13660  Delh=Delh+Y(I)*Integral(I)
13670  NEXT I
13680  Delh=Delh*F
13690  SUBEND
13700  !
13710  SUB Integral cp(T1,T2)
13720  !DETERMINE INTEGRAL OF CP*DELT OVER TEMP INTERVAL T1 TO T2, 'K
13730 Integral cp: !
13740  COM /Heat capacity/ Coef(*)
13750  COM /Energy/ Gf(*),Hf(*),Integral(*)
13760  Delt=(T2-T1)
13770  Delt2=(T2^2-T1^2)/2
13780  Delt3=(T2^3-T1^3)/3
13790  Delt4=(T2^4-T1^4)/4
13800  FOR I=1 TO 8
13810  Integral(I)=Coef(I,1)*Delt+Coef(I,2)*Delt2+Coef(I,3)*Delt3+Coef(I,4)*Delt
4
13820  NEXT I
13830  SUBEND
13840  !
13850  SUB Gas combustion(Y(*),F,T1,T2,O2,Avail ht)
13860  !DETERMINE AVAILABLE HEAT FROM COMBUSTION OF F M OF SYNGAS, SET F=1
13870  !Y(*): GAS STREAM; T1:INLET TEMP, 'C; T2:OUTLET TEMP, 'C; O2:STACK O2, DR
Y BASIS, FRACTION; AVAIL HT:AVAILABLE HEAT FROM COMBUSTION
13880  COM Ytemp(*)
```

```
13890  COM /Energy/ Gf(*),Hf(*),Integral(*)
13900  INTEGER I,J
13910 Gas combustion: !
13920  !DETERMINE AIR FLOW AND OUTLET COMPOSITION
13930  Io2=.5*Y(1)+1.5*Y(3)+.5*Y(4)+2*Y(6)-Y(8)
13940  In2=.79/.21*Io2
13950  X=O2*(Y(1)+Y(2)+Y(3)+Y(6)+Y(7)+In2)/(1-(1+.79/.21)*O2)
13960  !YTEMP(I) IS THE MOLAR FLOW OF COMPONENT I IN THE FLUE GAS/MOLE OF COMBUS
TION GAS
13970  FOR I=1 TO 8
13980  Ytemp(I)=0
13990  NEXT I
14000  Ytemp(2)=Y(1)+Y(2)+Y(3)+Y(6)
14010  Ytemp(5)=2*Y(3)+Y(4)+Y(5)+2*Y(6)
14020  Ytemp(7)=Y(7)+.79/.21*(Io2+X)
14030  Ytemp(8)=X
14040  !DETERMINE MOLAR FLOW OF FLUE GAS /MOLE OF COMBUSTION GAS
14050  Fflue=0
14060  FOR I=1 TO 8
14070  Fflue=Ytemp(I)+Fflue
14080  NEXT I
14090  Fflue=Fflue*F
14100  !CONVERT YTEMP(I) TO MOLE FRACTION
14110  FOR I=1 TO 8
14120  Ytemp(I)=Ytemp(I)/Fflue
14130  NEXT I
14140  !DETERMINE HEAT OF COMBUSTION AT REFERENCE TEMP, 298 K
14150  Tref=298
14160  Delhinit1=Hf(2)-Hf(1)
14170  Delhinit3=Hf(2)+2*Hf(5)-Hf(3)
14180  Delhinit4=Hf(5)
14190  Delhinit6=Hf(2)+2*Hf(5)-Hf(6)
14200  Ht comb=F*(Y(1)*Delhinit1+Y(3)*Delhinit3+Y(4)*Delhinit4+Y(6)*Delhinit6)
14210  !DETERMINE HEAT IN DUE TO FLOW OF FUEL, ASSUME COMBUSTION AIR IS AT REFER
ENCE TEMPERATURE
14220  CALL Heat content(Y(*),F,Tref,T1+273,In ht flow)
14230  !DETERMINE HEAT OUT DUE TO FLOW OF COMBUSTION PRODUCTS
14240  CALL Heat content(Ytemp(*),Fflue,Tref,T2+273,Out ht flow)
14250  !DETERMINE AVAILABLE HEAT FROM COMBUSTION
14260  Avail ht=In ht flow-Ht comb-Out ht flow
14270  SUBEND
14280  !
14290  SUB Process print
14300  !CALLING SUB FOR PRINT SUBROUTINES
14310 Process print: !
14320  COM /Composition/ Yinr(*),Yfr(*),Yinco(*),Yfco(*),Yinacid(*),Yfacid(*),Yi
nm(*),Yfm(*),Yrm(*),Ymm(*)
14330  COM /Flows/ Finr,Ffr,Finco,Ffco,Finacid,Ffacid,Finm,Ffm,Frm,Fmm,Fpm
14340  COM /Gasifier/ Fwood,Fsteam,Fchar,Fo2,Fh2o,Fcond,Fgas,Ygas(*),Fgasifier,Y
gasifier(*),Twood,Tsteam,Tgas,To2,Char yield,Ext ht supply,Gasifier$
14350  COM /Wood/ Wood(*),Subc,Subh,Subo,Mwood,Hfwood
```

```
14360  PRINTER IS 701
14370  CALL Prt dryer
14380  CALL Prt gasifier
14390 CALL Prt syngas(Ygas(*),Fgas)
14400 CALL Prt reformer
14410 CALL Prt co shift
14420 CALL Prt acid rem
14430 CALL Prtmethanol(Yfacid(*),Ffacid)
14440 CALL Prt compression
14450 CALL Prt oxygen
14460 CALL Prt boiler
14470 CALL Prt efficiency
14480 CALL Prt plant cap(Gasifier$)
14490 CALL Prt operating
14500 CALL Prt supply
14510 BEEP
14520 PRINTER IS 1
14530 SUBEND
14540 !
14550 SUB Eqn state(Y(*),T,P,Z)
14560 Eqn state:!
14570 !DETERMINE THE COMPRESSIBILITY FACTOR FOR A GAS MIXTURE
14580  COM /Data storage/ A(*)
14590  COM /Critical/ Critical(*)
14600  !DATA STORAGE IS USED AS TEMPORARY STORAGE ARRAY FOR INTERMEDIATE CALC
14610  INTEGER I,J
14620  !DETERMINE REDUCED PRESSURE AND TEMPERATURE
14630  GOTO Bypass1
14640  Crit t=0
14650  Crit p=0
14660  FOR I=1 TO 8
14670  Crit t=Crit t+Y(I)*Critical(1,I)
14680  Crit p=Crit p+Y(I)*Critical(2,I)
14690  NEXT I
14700  PRINT "CRIT T=";Crit t,"CRIT P=";Crit p
14710  Red t=T/Crit t
14720  Red p=P/Crit p
14730  PRINT "RED T=";Red t,"RED P=";Red p
14740 Bypass1: !
14750  R=82.0567
14760  Pseudoa=.4278*R^2
14770  Pseudob=.0867*R
14780  FOR I=1 TO 8
14790  A(1,I)=Pseudoa*Critical(1,I)^2.5/Critical(2,I)
14800  A(2,I)=Pseudob*Critical(1,I)/Critical(2,I)
14810  NEXT I
14820  Aa=0
14830  Bb=0
14840  FOR I=1 TO 8
14850  Aa=Aa+Y(I)*A(1,I)^.5
14860  Bb=Bb+Y(I)*A(2,I)
```

```
14870  NEXT I
14880  Aa=Aa^2
14890  Coefa=Aa/(R^2*T^2.5)
14900  Coefb=Bb/(R*T)
14910  Coefc=Coefb^2*P^2+Coefb*P-Coefa*P
14920  Coefd=Coefa*Coefb*P^2
14930  Z=1
14940 Again: !
14950  F=Z^3-Z^2-Coefc*Z-Coefd
14960  Derf=3*Z^2-2*Z-Coefc
14970  Zn=Z-F/Derf
14980  IF (ABS(Z-Zn)<Z/100) THEN GOTO Finish
14990  Z=Zn
15000  GOTO Again
15010 Finish: !
15020  SUBEND
15030  !
15040  SUB Compressor(Y(*),F,T1,T2,P1,P2,Hcomp)
15050 Compressor: !
15060  COM /Heat capacity/ Coef(*)
15070  INTEGER I,J
15080  !DETERMINE THE SHAFT POWER REQUIREMENTS ASSUMING POLYTROPIC COMPRESSION
15090    !NUP:POLYTROPIC EFFICIENCY, ELLIOT COMPRESSOR FRAME 29M ASSUMED
15100    !NUBS:EFFICIENCY DUE TO BEARING AND SEAL LOSSES, ASSUMED VALUE USED
15110    !HCOMP:SHAFT POWER, CAL/s
15120  R=1.9872
15130  Nup=.76
15140  Nubs=.96
15150  !DETERMINE AVG Cp AT INLET TEMPERATURE
15160  Cp mix=0
15170  FOR I=1 TO 8
15180  Cp i=Y(I)*(Coef(I,1)+Coef(I,2)*T1+Coef(I,3)*T1^2+Coef(I,4)*T1^3)
15190  Cp mix=Cp mix+Cp i
15200  NEXT I
15210  !DETERMINE COMPRESSIBILITY FACTOR
15220  CALL Eqn state(Y(*),T1,P1,Z1)
15230  Zavg=Z1
15240 Again: !
15250  !DETERMINE ADIABATIC EXPONENT
15260  Kmix=Cp mix/(Cp mix-R)
15270  !POLYTROPIC EXPONENT IS DETERMINED USING KMIX AND NUP
15280  !   (N-1)/N=(KMIX-1)/(KMIX*NUP)
15290  Pseudon=(Kmix-1)/(Kmix*Nup)
15300  !DETERMINE POLYTROPIC HEAD
15310  Hp=Zavg*R*T1*((P2/P1)^Pseudon-1)/Pseudon
15320  !DETERMINE DISCHARGE TEMP
15330  T2=Hp*Pseudon/(Zavg*R)+T1
15340  CALL Eqn state(Y(*),T2,P2,Z2)
15350  IF (ABS(Zavg-Z2)<Zavg/100) THEN GOTO Finish
15360  Zavg=(Z1+Z2)/2
15370  Cp mix=0
```

```
15380  FOR I=1 TO 8
15390  Cp i=Y(I)*(Coef(I.1)+Coef(I.2)*T2+Coef(I.3)*T2^2+Coef(I.4)*T2^3)
15400  Cp mix=Cp mix+Cp i
15410  NEXT I
15420  GOTO Again
15430 Finish: !
15440  Hcomp=(F*Hp)/(Nup*Nubs)
15450  SUBEND
15460  !
15470  SUB Prt compression
15480 Prt compression: !
15490  COM /Compression/ Hcomp(*)
15500  !HCOMP(I.1)=SHAFT POWER. CAL/t
15510  !HCOMP(I.2)=INLET TEMP. 'C
15520  !HCOMP(I.3)=OUTLET TEMP. 'C:CALCULATED
15530  !HCOMP(I.4)=INLET PRESSURE. ATM
15540  !HCOMP(I.5)=OUTLET PRESSURE.ATM
15550  !I=COMPRESSOR DESIGNATOR
15560  PRINT "COMPRESSION:"
15570  PRINT USING "15A";"METHANOL UNIT:"
15580  PRINT USING "20X.8A.5X.8A";"INLET"."RECYCLE"
15590  PRINT USING "20A.4D.2D.5X.4D.2D";"SHAFT POWER. CAL/T:".Hcomp(1.1).Hcomp(2
.1)
15600  PRINT USING "20A.4D.2D.5X.4D.2D";"INLET TEMP. 'C:".Hcomp(1.2).Hcomp(2.2)
15610  PRINT USING "20A.4D.2D.5X.4D.2D";"OUTLET TEMP. 'C:".Hcomp(1.3).Hcomp(2.3)
15620  PRINT USING "20A.4D.2D.5X.4D.2D";"INLET PRESS. ATM:".Hcomp(1.4).Hcomp(2.4
)
15630  PRINT USING "20A.4D.2D.5X.4D.2D";"OUTLET PRESS. ATM:".Hcomp(1.5).Hcomp(2.
5)
15640  PRINT "  "
15650  PRINT "  "
15660  SUBEND
15670  !
15680  SUB Gasifier(Y(*).F.Char yield.Tsteam.Tgas.Fwood.Fsteam.Fchar.Fo2.Fh2o.Fc
ond.Fgasifier.Ygasifier(*).Ext ht supply.Type$)
15690  COM /Energy/ Gf(*).Hf(*).Integral(*)
15700  COM /Wood/ Wood(*).Subc.Subh.Subo.Mwood.Hfwood
15710 Gasifier: !
15720  !WOOD CHARACTERISITICS
15730  !DETERMINE HHV ON ASH AND N2 FREE BASIS
15740  Anfb=(Wood(4)+Wood(5))/100
15750  Mwood=100*(1-Anfb)
15760  Hhv=Wood(7)/(1-Anfb)
15770  !DETERMINE MOLECULAR FORMULA FOR WOOD. MW=100-ASH-N
15780  Subc=Wood(1)/12
15790  Subh=Wood(2)
15800  Subo=Wood(3)/16
15810  !DETERMINE HEAT OF FORMATION OF WOOD AT 25'C
15820  Hfwood=Hhv*Mwood+Subc*Hf(2)+Subh/2*(-68317)
15830  !MASS BALANCE
15840  !DETERMINE Fwood AND FCHAR BASED ON C-BALANCE
```

```
15850  Fcond=0
15860  Fwood=F*(Y(1)+Y(2)+Y(3)+Y(8))/(Subc-Mwood*Char yield/12)
15870  Fchar=Fwood*Mwood*Char yield/12
15880  !DETERMINE FSTEAM FROM H BALANCE
15890  !DETERMINE H2O1 INTRODUCED AS MC OF WOOD
15900  Fh2o=Fwood*Mwood*Wood(6)/(1800*(1-Wood(6)/100))
15910  Fsteam=(F*(4*Y(3)+2*Y(4)+2*Y(5)+4*Y(6))-Fwood*Subh-2*Fh2o)/2
15920  IF (Fsteam>0) THEN GOTO Bypass
15930  !STEAM CONDENSATION HAS OCCURRED IN GAS PHASE. Y(*):ADJUST
15940  !DETERMINE FCOND AND GAS COMPOSITION EX GASIFIER
15950  CALL Gasifier water(Y(*),F,Fsteam,Fcond)
15960 Bypass: !
15970  !DETERMINE FO2 FROM O2 BALANCE
15980  Fo2=(F*(Y(1)+2*Y(2)+Y(3)+Y(5)+2*Y(8))-Fwood*Subo-Fsteam-Fh2o)/2
15990  !SPECIFIY GAS COMPOSITION AND FLOW FROM GASIFIER
16000  FOR I=1 TO 8
16010  Ygasifier(I)=Y(I)
16020  NExT I
16030  Fgasifier=F
16040  !DETERMINE OVERALL HEAT OF REACTION AT 298 'K
16050  !DETERMINE HEAT OF FORMATION OF GAS
16060  Heat=0
16070  FOR I=1 TO 8
16080  Heat=Hf(I)*Y(I)+Heat
16090  NEXT I
16100  Heat=Heat*F
16110  !DETERMINE THE OVERALL HEAT OF REACTION AT 298 'K
16120  Ht react=Heat-Fsteam*Hf(5)-Fwood*Hfwood+68317*Fh2o
16130  !DETERMINE HEAT IN DUE TO FLOW OF REACTANTS
16140  !  ASSUME WOOD AND O2 ARE INTRODUCED AT THE REF TEMP FOR PRESENT
16150  CALL Integral cp(298,Tsteam+273)
16160  Steam ht in=Integral(5)*Fsteam
16170  !DETERMINE HEAT OUT DUE TO SYNGAS GAS FLOW
16180  CALL Heat content(Y(*),F,298,Tgas+273,Gas ht out)
16190  !DETERMINE HEAT OUT DUE TO CHAR, AT SAME TEMP AS GAS
16200  Char ht out=Fchar*(2.673*(Tgas-298)+2.617E-3*(Tgas^2-298^2)/2+1.163E+5*(1
/Tgas-1/298))
16210  !DETERMINE EXTERNAL HT SUPPLY REQUIRED
16220  Ext ht supply=Gas ht out+Char ht out+Ht react-Steam ht in
16230  !ADJUST FCHAR AND EXT HT SUPPLY IF BCL GASIFIER USED
16240  IF (Type$="Bcl") THEN GOTO Bcl comb
16250  GOTO Finish gasifier
16260 Bcl comb: !
16270  CALL Bcl combustor(Fchar,Tgas,.05,Ext ht supply)
16280 Finish gasifier: !
16290  SUBEND
16300  !
16310  SUB Gasifier water(Y(*),F,Fsteam,Fcond)
16320 Gasifier water: !
16330  INTEGER I
16340  !FSTEAM DETERMINED BY MASS BALANCE IS < 0
```

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16350  !WATER HAS BEEN CONDENSED OUT OF GAS
16360  !DETERMINE WET GAS COMPOSITION
16370  Fcond=-Fsteam
16380  Y(5)=Y(5)+Fcond
16390  !NORMALIZE GAS COMPOSITION
16400  F=0
16410  FOR I=1 TO 8
16420  F=F+Y(I)
16430  NEXT I
16440  FOR I=1 TO 8
16450  Y(I)=Y(I)/F
16460  NEXT I
16470  SUBEND
16480  !
16490  SUB Prt gasifier
16500 Prt gasifier: !
16510  COM /Gasifier/ Fwood,Fsteam,Fchar,Fo2,Fh2o,Fcond,Fgas,Ygas(*),Fgasifier,Y
gasifier(*),Twood,Tsteam,Tgas,To2,Char yield,Ext ht supply,Gasifier$
16520  COM /Wood/ Wood(*),Subc,Subh,Subo,Mwood,Hfwood
16530  PRINT "GASIFIER:";Gasifier$
16540  PRINT USING "2X,15A";"FLOWS, M/t:"
16550  PRINT USING "2X,10A,2D.4D,2X,1A,3D.2D,4A";"DRY WOOD=";Fwood,"(",Fwood*Mwo
od,"g/t)"
16560  PRINT USING "2X,10A,2D.4D";"MOISTURE=";Fh2o
16570  PRINT USING "2X,10A,2D.4D";"STEAM=";Fsteam
16580  PRINT USING "2X,10A,2D.4D";"OXYGEN=";Fo2
16590  PRINT USING "2X,18A,2D.4D";"GAS FROM GASIFIER=";Fgasifier
16600  PRINT USING "2X,15A,2D.4D";"GAS TO PROCESS=";Fgas
16610  PRINT USING "2X,10A,2D.4D,2X,6A,2D.4D";"CHAR=";Fchar,"YIELD=",Char yield
16620  PRINT USING "2X,28A,2D.4D";"STEAM CONDENSATION FROM GAS=";Fcond
16630  PRINT USING "28A,6D.2D";"EXTERNAL HEAT SUPPLY, CAL/T=";Ext ht supply
16640  PRINT "GAS COMPOSITION:"
16650  PRINT USING "10X,15A,5X,15A";"EX GASIFIER","TO PROCESS"
16660  PRINT USING "5A,5X,2D.4D,13X,2D.4D";"CO:",Ygasifier(1),Ygas(1)
16670  PRINT USING "5A,5X,2D.4D,13X,2D.4D";"CO2:",Ygasifier(2),Ygas(2)
16680  PRINT USING "5A,5X,2D.4D,13X,2D.4D";"CH3OH:",Ygasifier(3),Ygas(3)
16690  PRINT USING "5A,5X,2D.4D,13X,2D.4D";"H2:",Ygasifier(4),Ygas(4)
16700  PRINT USING "5A,5X,2D.4D,13X,2D.4D";"H2O:",Ygasifier(5) Ygas(5)
16710  PRINT USING "5A,5X,2D.4D,13X,2D.4D";"CH4:",Ygasifier(6),Ygas(6)
16720  PRINT USING "5A,5X,2D.4D,13X,2D.4D";"N2:",Ygasifier(7),Ygas(7)
16730  PRINT USING "5A,5X,2D.4D,13X,2D.4D";"O2:",Ygasifier(8),Ygas(8)
16740  PRINT "TEMPERATURES: C"
16750  PRINT USING "2X,13A,3D.1D";"WOOD AND O2=",25
16760  PRINT USING "2X,13A,3D.1D";"STEAM=",Tsteam
16770  PRINT USING "2X,13A,3D.1D";"GAS AND CHAR=",Tgas
16780  PRINT "WOOD COMPOSITION, ASH AND N2 FREE BASIS:"
16790  PRINT USING "2X,2A,2D.3D";"C=",Wood(1),"H=",Wood(2),"O=",Wood(3),"N=",Woo
d(4)
16800  PRINT USING "2X,4A,4D.3D";"ASH=",Wood(5),"HHV=",Wood(7)
16810  PRINT USING "2X,5A,2D.3D";"SUBC=",Subc,"SUBH=",Subh,"SUBO=",Subo
16820  PRINT USING "2X,7A,3D.2D";"MOL WT=",Mwood
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16830  PRINT "  "
16840  PRINT "  "
16850  SUBEND
16860  !
16870  SUB Solid combustn(Tref.Texit.O2.X.Y.Z.Mw.Mc.Heat form.Avail ht)
16880  COM /Energy/ Gf(*).Hf(*).Integral(*)
16890 Solid combustn: !
16900  !DETERMINE AVAILABLE HT FROM THE COMBUSTION OF WET WOOD. BASED ON 1 M OF
DRY WOOD FLOW
16910  !TREF:REF TEMP. TEXIT:OUTLET TEMP;  °K
16920  !O2:STACK O2. DRY BASIS. FRACTION
16930  !DETERMINE MOLAR OUTLET FLOWS
16940  Moisture=Mw*Mc/(1800*(1-Mc/100))
16950  Fouto2=O2*(X+Y/2+Moisture+.79/.21*(X+Y/4-Z/2))/(1-O2*(1+.79/.21))
16960  Foutn2=(Fouto2+X+Y/4-Z/2)*.79/.21
16970  Fouth2o=Y/2+Moisture
16980  Foutco2=X
16990  !DETERMINE HEAT OF REACTION AT 298 °K
17000  Ht react=X*Hf(2)+(Y/2+Moisture)*Hf(5)-Heat form-Moisture*Hf(9)
17010  !ASSUME REACTANTS ARE AT REF TEMP THEREFORE NO HEAT IN DUE TO FLOW
17020  !HEAT OUT DUE TO FLOW OF PRODUCTS
17030  CALL Integral cp(Tref.Texit)
17040  Ht out flow=Foutco2*Integral(2)+Fouth2o*Integral(5)+Foutn2*Integral(7)+Fo
uto2*Integral(8)
17050  !DETERMINE AVAIL HT FROM HT BAL
17060  Avail ht=-Ht react-Ht out flow
17070  SUBEND
17080  !
17090  SUB Dryer
17100  COM /Energy/ Gf(*).Hf(*).Integral(*)
17110  COM /Wood/ Wood(*).Subc.Subh.Subo.Mwood.Hfwood
17120  COM /Gasifier/ Fwood.Fsteam.Fchar.Fo2.Fh2o.Fcond.Fgas.Ygas(*).Fgasifier.Y
gasifier(*).Twood.Tsteam.Tgas.To2.Char yield.Ext ht supply.Gasifier$
17130  COM /Dryer/ Ffdry wood.Fdryer wood.Tdryer.Dryer stack o2.Fevap
17140 Dryer: !
17150  !DETERMINE FEED OF WOOD TO DRYER AND QUANTITY OF DRY FEED USED FOR COMBUS
TION TO PROVIDE HEAT FOR THE PROCESS
17160  A=Mwood*Wood(8)/(1800*(1-Wood(8)/100))
17170  B=Mwood*Wood(6)/(1800*(1-Wood(6)/100))
17180  CALL Solid combustn(298.Tdryer+273.Dryer stack o2.Subc.Subh.Subo.Mwood.Wo
od(6).Hfwood.Avail ht)
17190  !FFDRY WOOD: QUANTITY OF WOOD USED FOR COMBUSTION. M/t
17200  Ffdry wood=(Fh2o-A*Fwood)/(A-B-Avail ht/(Hf(5)-Hf(9)))
17210  !FDRYER WOOD: QUANTITY OF WOOD FED TO DRYER. M/t
17220  Fdryer wood=Fwood+Ffdry wood
17230  !FEVAP:QUANTITY OF WATER EVAPORATED IN DRYER
17240  Fevap=Avail ht*Ffdry wood/(Hf(5)-Hf(9))
17250  SUBEND
17260  !
17270  SUB Prt dryer
17280  COM /Wood/ Wood(*).Subc.Subh.Subo.Mwood.Hfwood
```

```
17290  COM /Gasifier/ Fwood,Fsteam,Fchar,Fo2,Fh2o,Fcond,Fgas,Ygas(*),Fgasifier,Y
gasifier(*),Twood,Tsteam,Tgas,To2,Char yield,Ext ht supply,Gasifier$
17300  COM /Dryer/ Ffdry wood,Fdryer wood,Tdryer,Dryer stack o2,Fevap
17310 Prt dryer: !
17320  PRINT "PRETREATMENT:"
17330  PRINT USING "2X,10A";"DRYER:"
17340  PRINT USING "4X,35A,3D.3D,3A,3X,1A,3D.3D,4A";"FEED TO DRYER (DRY WOOD):",
Fdryer wood,"M/t","(",Fdryer wood*Mwood,"g/t)"
17350  PRINT USING "4X,35A,3D.3D,3A,3X,1A,3D.3D,4A";"FEED TO GASIFIER (DRY WOOD)
:",Fwood,"M/t","(",Fwood*Mwood,"g/t)"
17360  PRINT USING "4X,35A,3D.3D,3A,3X,1A,3D.3D,4A";"DRYER PRODUCT COMBUSTED (DR
Y WOOD):",Ffdry wood,"M/t","(",Ffdry wood*Mwood,"g/t)"
17370  PRINT USING "4X,20A,3D.3D,3A";"WATER EVAPORATED:",Fevap,"M/t"
17380  PRINT USING "4X,35A";"MOISTURE CONTENT (WET BASIS, %):"
17390  PRINT USING "6X,15A,3D.3D";"FEED TO DRYER:",Wood(8)
17400  PRINT USING "6X,15A,3D.3D";"DRYER PRODUCT:",Wood(6)
17410  PRINT USING "4X,15A,3D.3D";"STACK O2, %:",Dryer stack o2*100
17420  PRINT "  "
17430  PRINT "  "
17440  SUBEND
17450  !
17460  SUB Oxygen(F,Power)
17470 Oxygen: !
17480  !DETERMINE THE POWER REQUIREMENTS FOR O2 PRODUCTION
17490  !USE DATA FROM MOLTEN SALT REPORT
17500  !CRYOGENIC O2 PRODUCTION:14138 CAL/M O2
17510  Power=14138*F
17520  SUBEND
17530  !
17540  SUB Prt oxygen
17550 Prt oxygen: !
17560  COM /Oxygen/ Power
17570  PRINT "OXYGEN PRODUCTION:"
17580  PRINT "  CYROGENIC PROCESS"
17590  PRINT USING "2X,20A,6D.3D,5A";"POWER REQUIREMENTS=",Power,"CAL/t"
17600  PRINT "  "
17610  PRINT "  "
17620  SUBEND
17630  !
17640  SUB Turbina(Tlower steam,Thigher steam,Comp power,Turbine eff,Heat duty,F
steam boiler)
17650  COM /Energy/ Gf(*),Hf(*),Integral(*)
17660 Turbine: !
17670  !DETERMINE STEAM FLOW REQUIRED BY BOILER, STEAM TURBINE USED TO POWER COM
PRESSORS
17680  !CORRELATION FOR STEAM APPLIES ONLY AT ATM PRESSURE THEREFORE ENTHALPY VA
LUES ARE APPROXIMATE
17690  !Tlower steam: TEMPERATURE OF STEAM DISCHARGED FROM TURBINE-ASSUME SATURA
TED VALUE (TYPICAL VALUE: 250 psig, 550 'F)
17700  !Thigher steam: TEMPERATURE OF STEAM FED TO TURBINE-ASSUME SAME AS DISCHA
RGED FROM BOILER (TYPICAL VALUE: 650 psig, 750 'F)
```

```
17710  !COMP POWER: TOTAL COMPRESSOR POWER REQUIRED. CAL/t
17720  !TURBINE EFF: TURBINE EFFICIENCY-DEPENDS UPON DESIGN-ASSUME 0.75
17730  !HEAT DUTY: STEAM ENTHALPY REQUIREMENT. CAL/t
17740  !Fsteam boiler: STEAM PRODUCTION REQUIREMENTS FROM BOILER. M/t
17750  CALL Integral cp(Tlower steam+273,Thigher steam+273)
17760  Heat duty=Comp power/Turbine eff
17770  Fsteam boiler=Comp power/(Turbine eff*Integral(5))
17780  SUBEND
17790  !
17800  SUB Solid mix(Fboiler wood,Mwood,Mcwood,Fchar,Mc char,Subc,Subh,Subo,X,Mc
 new,Mw new)
17810 Solid mix: !
17820  !DETERMINE THE MOISTURE CONTENT, COMPOSITION AND MOLECULAR WEIGHT OF A ST
REAM COMPOSED OF WOOD AND CHAR
17830  X=(Fboiler wood*Subc+Fchar)/Fboiler wood
17840  !DETERMINE NEW MC
17850  Fboiler h2o=Fwood boiler*Mwood*Mcwood/(100*(1-Mcwood/100))
17860  Fchar h2o=12*Fchar*Mc char/(100*(1-Mc char/100))
17870  IF (Fwood+Fchar=0) THEN GOTO Mix bypass
17880  Mc new=(Fboiler h2o+Fchar h2o)*100/(Fboiler h2o+Fchar h2o+Fwood*Mwood+Fch
ar*12)
17890  GOTO Mix bypass1
17900 Mix bypass: !
17910  Mc new=Mcwood
17920 Mix bypass1: !
17930  Mw new=12*X+Subh+16*Subo
17940  SUBEND
17950  !
17960  SUB Boiler(Fboiler wood,Mw,Mcwood,Fc,Mc char,Subc,Subh,Subo,Tls,Ths,Comp
power,Turbine eff,Boiler stack o2,Hfwood,Avail ht,Fst,Ext ht,Fsteam)
17970  COM /Energy/ Gf(*),Hf(*),Integral(*)
17980  ! FST=FSTEAM BOILER, DETERMINED IN TURBINE SUBPROGRAM
17990 Boiler: !
18000  Mwood=Mw
18010  Fchar=Fc
18020  Tlower steam=Tls
18030  Thigher steam=Ths
18040  !DETERMINE WOOD FEED REQUIRED TO PRODUCE STEAM FOR TURBINE DRIVE FOR COMP
RESSORS IN METHANOL UNIT AND POWER FOR O2 PRODUCTION
18050  !THIGHER STEAM: STEAM TEMPERATURE EX BOILER
18060  !TLOWER STEAM: STEAM TEMPERATURE EX TURBINE
18070  CALL Turbine(Tlower steam,Thigher steam,Comp power,Turbine eff,Heat duty,
Fst)
18080  X=Subc
18090  Y=Subh
18100  Z=Subo
18110  !DETERMINE FWOOD BOILER USING NEWTON RAPHSON ITERATION
18120  Fboiler wood=0
18130  X1=Fboiler wood
18140  Avail ht=0
18150  IF (Fchar=0) THEN GOTO Char bypass
```

```
18160  CALL Solid combustn(298,Thigher steam+273,Boiler stack o2,1,0,0,12,50,0,A
vail ht)
18170  Avail ht=Avail ht*Fchar
18180  IF (Avail ht>Heat duty) THEN GOTO Finish
18190  F1=Heat duty-Avail ht
18200 Boiler repeat: !
18210  !DETERMINE DERIVATIVE
18220  Fboiler wood=Fboiler wood+.0001
18230  CALL Solid mix(Fboiler wood,Mwood,Mcwood,Fchar,Mc char,Subc,Subh,Subo,X,M
c new,Mw new)
18240  CALL Solid combustn(298,Thigher steam+273,Boiler stack o2,X,Y,Z,Mw new,Mc
 new,Hfwood,Avail ht)
18250  Avail ht=Avail ht*Fboiler wood
18260  X2=Fboiler wood
18270  F2=Heat duty-Avail ht
18280  CALL Newton raphson(X1,F1,X2,F2,Xnew)
18290  Fboiler wood=Xnew
18300  CALL Solid mix(Fboiler wood,Mwood,Mcwood,Fchar,Mc char,Subc,Subh,Subo,X,M
c new,Mw new)
18310  CALL Solid combustn(298,Thigher steam+273,Boiler stack o2,X,Y,Z,Mw new,Mc
 new,Hfwood,Avail ht)
18320  Avail ht=Avail ht*Fboiler wood
18330  IF (ABS(Avail ht-Heat duty)<Heat duty/500) THEN GOTO Finish
18340  X1=Fboiler wood
18350  F1=Heat duty-Avail ht
18360  GOTO Boiler repeat
18370 Char bypass: !
18380  CALL Solid combustn(298,Thigher steam+273,Boiler stack o2,Subc,Subh,Subo,
Mwood,Mcwood,Hfwood,Avail ht)
18390  Fboiler wood=Heat duty/Avail ht
18400 Finish: !
18410  SUBEND
18420  !
18430  SUB Prt boiler
18440 Prt boiler: !
18450  COM /Boiler/ Fboiler wood,Tlower steam,Thigher steam,Boiler stack o2,Turb
ine eff,Avail ht,Mc char,Fsteam boiler
18460  COM /Gasifier/ Fwood,Fsteam,Fchar,Fo2,Fh2o,Fcond,Fgas,Ygas(*),Fgasifier,Y
gasifier(*),Twood,Tsteam,Tgas,To2,Char yield,Ext ht supply,Gasifier$
18470  PRINT "BOILER"
18480  PRINT "  FEED M/t, DRY BASIS:"
18490  PRINT USING "4X,5A,3D.3D,2X,5A,3D.3D";"WOOD=";Fboiler wood,"CHAR=";Fchar
18500  PRINT USING "4X,12A,3D.3D";"MC CHAR, %=";Mc char
18510  PRINT USING "2X,16A,3D.3D";"STEAM FLOW, M/t=",Fsteam boiler
18520  PRINT "  STEAM TEMPERATURES, 'C:"
18530  PRINT USING "4X,25A,3D.3D";"BOILER HIGH TEMP STEAM=",Thigher steam
18540  PRINT USING "4X,25A,3D.3D";"TURBINE OUTLET=",Tlower steam
18550  PRINT USING "2X,12A,3D.3D";"STACK O2, %=",Boiler stack o2*100
18560  PRINT USING "2X,12A,3D.3D";"TURBINE EFF=",Turbine eff
18570  PRINT " "
18580  PRINT " "
```

```
18590  SUBEND
18600  !
18610  SUB Efficiency(Ymm,Fm,Fwood dryer,Fwood boiler,Subc,Mwood,Hvwood,Anf,C co
nv,First law)
18620  !DETERMINE THE CARBON CONVERSION TO PRODUCT AND FIRST LAW EFFICIENCY
18630 Efficiency: !
18640  C conv=Ymm*Fm*100/((Fwood dryer+Fwood boiler)*Subc)
18650  First law=C conv*173650*(1-Anf)*Subc/(Mwood*Hvwood)
18660  SUBEND
18670  !
18680  SUB Prt efficiency
18690  COM /Efficiency/ C conv,First law
18700  !PRINT OVERALL EFFICIENCY OF CONVERSION OF BIOMASS TO METHANOL
18710 Prt efficiency: !
18720  PRINT "OVERALL CONVERSION EFFICIENCY"
18730  PRINT USING "2X,16A,3D.3D";"C CONVERSION, %=",C conv
18740  PRINT USING "2X,17A,3D.3D";"FIRST LAW EFF. %=",First law
18750  PRINT "  "
18760  PRINT "  "
18770  SUBEND
18780  !
18790  SUB Plant capital(Mw,Target,Fdryer wd,Fwood,Fgasin,Ygasin,Ffr,Yfr,Finco,Y
inco,Foco,Yoco,Finacid,Yinacid,Ffacid,Yfacid,Fmm,Ymm,Fo2,Power,Fsteam boiler,G$)
18800  COM /Capital1/ Pwood prep,Wood prep,Pgasifier,Gasifier,Po2,Oxygen,Preform
er,Reformer,Pshift,Co shift,Premoval,Removal,Methanol,Pcomp,Comp,Pboiler
18810  COM /Capital2/ Boiler,Misc offsite,Blcc,Offsite,Plant
18820  !DETERMINE THE TOTAL CAPITAL COST OF INDIRECT LIQ PLANT
18830 Plant capital:
18840  Gasifier$=G$
18850  !SPECIFY METHANOL PRODUCTION COSTS
18860  Mech=Fmm*Ymm*3.2E-5
18870  Mult=Target/Mech
18880  !DETERMINE WOOD PREP COST
18890  Pwood prep=(Fdryer wood*Mw*Mult)/24000
18900  Wood prep=11675*Pwood prep^.555
18910  !DETERMINE GASIFIER COST
18920  Pgasifier=Fwood*Mw*Mult/24000
18930  IF (Gasifier$="Mltsalt") THEN GOTO Mltsalt
18940  IF (Gasifier$="Seri") THEN GOTO Seri
18950  IF (Gasifier$="Pnl") THEN GOTO Pnl
18960  IF (Gasifier$="Bcl") THEN GOTO Bcl
18970  IF (Gasifier$="Fluid bed") THEN GOTO Fluid bed
18980  PRINT "GASIFIER SPEC PROBLEM"
18990  STOP
19000 Mltsalt:
19010  A=5834
19020  B=.7443
19030  GOTO Gasby
19040 Seri:
19050  A=852
19060  B=.8854
```

```
19070  GOTO Gasby
19080 Pnl: !
19090  A=119
19100  B=1.1008
19110  GOTO Gasby
19120 Bcl: !
19130  A=2468
19140  B=.8082
19150  GOTO Gasby
19160 Fluid bed: !
19170  A=9149
19180  B=.6347
19190 Gasby: !
19200  Gasifier=A*Pgasifier^B
19210  !DETERMINE O2 COSTS
19220  Po2=Fo2*32*Mult/24000
19230  IF (Po2<2.0E+4) THEN GOTO Wan
19240  Oxygen=222.6*Po2^1.059
19250  GOTO O2by
19260 Wan: !
19270  Oxygen=35368*Po2^.6336
19280 O2by: !
19290  !DETERMINE REFORMER COSTS
19300  Preformer=(Fgasin*Ygasin-Ffr*Yfr)*Mult/24
19310  Reformer=744.6*Preformer^.628
19320  !DETERMINE CO SHIFT COSTS
19330  !IF FINCO=0 THEN NO CO SHIFT IS REQUIRED
19340  IF (Finco=0) THEN GOTO Bypassco
19350  Pshift=(Finco*Yinco-Foco*Yoco)*Mult/24
19360  Co shift=30151*Pshift^.42
19370  GOTO Cofinish
19380 Bypassco: !
19390  Co shift=0
19400 Cofinish: !
19410  !DETERMINE ACID GAS REMOVAL COSTS
19420  Premoval=(Finacid*Yinacid-Ffacid*Yfacid)*Mult/24
19430  Removal=5453*Premoval^.5506
19440  !DETERMINE METHANOL SYN COSTS
19450  Methanol=1.915E+6*Target^.451
19460  !DETERMINE COMPRESSION COSTS
19470  Pcomp=Power*Mult/24
19480  Comp=4.7725*Pcomp^.6141
19490  !DETERMINE BOILER COSTS
19500  Pboiler=Fsteam boiler*Mult*18/(8.64E+7)
19510  Boiler=2.262E+6*Pboiler^.33
19520  !DETERMINE MISC OFFSITE COSTS
19530  Misc offsite=7.885E+6
19540  !DETERMINE BATTERY LIMIT CAPITAL COSTS
19550  Blcc=Wood prep+Gasifier+Oxygen+Reformer+Co shift+Acid removal+Methanol+Co
mp
19560  !DETERMINE OFFSITE COSTS
19570  Offsite=Boiler+Misc offsite
```

```
19580  !DETERMINE TOTAL PLANT CAPITAL, 15% CONTINGENCY
19590  Plant=1.15*(Blcc+Offsite)
19600  SUBEND
19610  !
19620  SUB Prt plant cap(Gasifier$)
19630 Prt plant cap: !
19640  COM /Capital1/ Pwood prep,Wood prep,Pgasifier,Gasifier,Po2,Oxygen,Preform
er,Reformer,Pshift,Co shift,Premoval,Removal,Methanol,Pcomp,Comp,Pboiler
19650  COM /Capital2/ Boiler,Misc offsite,Blcc,Offsite,Plant
19660  PRINT "PLANT CAPITAL COSTS, $CAN JAN 1/85"
19670  PRINT "GASIFIER: ";Gasifier$
19680  PRINT "BLCC=";Blcc
19690  PRINT "OFFSITE=";Offsite
19700  PRINT "TOTAL PLANT CAPITAL=";Plant
19710  PRINT "  "
19720  PRINT "  "
19730  SUBEND
19740  !
19750  SUB Operat maint(Fboiler wood,Fdryer wood,Mwood,Target,Fmm,Ymm,Gasifier$)
19760  COM /Operating/ Wood cost,Tot mat util,Tot labour,Capital,Total operating
19770  COM /Capital2/ Boiler,Misc offsite,Blcc,Offsite,Plant
19780 Operat maint: !
19790  !DETERMINE ANNUAL OPERATING AND MAINTENANCE COSTS, 8000 H/YR
19800  !DETERMINE RAW MATERIAL AND PURCHASED UTILITY (PROCESS AND COOLING WATER)
 COSTS:MAT UTIL
19810  !DETERMINE LABOUR COSTS: DIRECT, SUPERVISION, OVERHEAD: LABOUR
19820  IF (Gasifier$="Mltsalt") THEN GOTO Mltsalt
19830  IF (Gasifier$="Sari") THEN GOTO Sari
19840  IF (Gasifier$="Pnl") THEN GOTO Pnl
19850  IF (Gasifier$="Bcl") THEN GOTO Bcl
19860  Mat util=8.49E-3
19870  Labour=4.044E-3
19880  GOTO Matbv
19890 Mltsalt: !
19900  Mat util=5.557E-3
19910  Labour=4.994E-3
19920  GOTO Matbv
19930 Sari: !
19940  Mat util=5.099E-3
19950  Labour=5.609E-3
19960  GOTO Matbv
19970 Pnl: !
19980  Mat util=1.601E-2
19990  Labour=5.332E-3
20000  GOTO Matbv
20010 Bcl: !
20020  Mat util=8.490E-3
20030  Labour=4.044E-3
20040 Matbv: !
20050  Meoh=Fmm*Ymm*3.2E-5
20060  Wood flow=(Fdryer wood+Fboiler wood)*Mwood*Target/(Meoh*24000)
20070  Tot mat util=Wood flow*(Wood cost+Mat util)*8000.0
```

```
20080  Tot labour=2.5*Wood flow*Labour*8000.0
20090  !DETERMINE CAPITAL RELATED COSTS:MAINTENANCE=4%OF BLCC, GENERAL PLANT OVE
RHEAD=2.6%OF BLCC
20100  Capital=.066*Blcc
20110  Total operating=Tot mat util+Tot labour+Capital
20120  SUBEND
20130  !
20140  SUB Prt operating
20150  COM /Operating/ Wood cost,Tot mat util,Tot labour,Capital,Total operating
20160  PRINT "TOTAL OPERATING EXPENSES, $CAN JAN 1/85"
20170  PRINT "WOOD COST, $Kg(DRY)=";Wood cost
20180  PRINT "MATERIAL AND UTILITY COSTS=";Tot mat util
20190  PRINT "LABOUR=";Tot labour
20200  PRINT "CAPITAL RELATED=";Capital
20210  PRINT "TOTAL OPERATING=";Total operating
20220  PRINT "  "
20230  PRINT "  "
20240  SUBEND
20250  !
20260  SUB Supply price(Plant,Total operating,Target)
20270  COM /Price/ Supply price,Interest,Years
20280 Supply price: !
20290 !DETERMINE THE SUPPLY PRICE BASED ON PLANT CAPITAL COST (PLANT), TOTAL OPE
RATING COST (TOTAL OPERATING), DISCOUNTING FACTOR (INTEREST), OPERATING YEARS
20300 !ASSUME 1 YEAR CONSTRUCTION PERIOD AND CONSTANT PRODUCTION RATE AND OPERAT
ING COSTS
20310 ! SUPPLY PRICE: $/TONNE
20320 Present value=((1+Interest)^Years-1)/(Interest*(1+Interest)^Years)
20330 Supply price=(Plant/(1+Interest)+Total operating*Present value)/(Target*80
00.0/24*Present value)
20340 SUBEND
20350 !
20360 SUB Prt supply
20370 Prt supply:!
20380  COM /Price/ Supply price,Interest,Years
20390  PRINT "SUPPLY PRICE:"
20400  PRINT "YEARS=";Years
20410  PRINT "DISCOUNTING FACTOR, %=";Interest*100
20420  PRINT "SUPPLY PRICE, $/TONNE=";Supply price
20430  SUBEND
20440  !
20450  SUB Bcl combustor(Fchar,Tgas,Stack o2,Ext ht supply)
20460  !CHECK THAT NO PROBLEM WITH GASIFIER INPUT INFO: ie EXT HT SUPPLY
20470  IF (Ext ht supply<0.) THEN GOTO Finish2
20480  CALL Solid combustn(298,Tgas+273,Stack o2,1,0,0,12,0,0,Avail ht)
20490  !DETERMINE QUANTITY OF HEAT REQUIRED FOR HEAT
20500  Fchar required=Ext ht supply/Avail ht
20510  IF (Fchar required>Fchar) THEN GOTO Finish1
20520  Fchar=Fchar-Fchar required
20530  Ext ht supply=0.
20540  GOTO Finish2
```

```
20550 Finish1: !
20560  Ext ht supply=Ext ht supply-Fchar*Avail ht
20570  Fchar=0.
20580 Finish2: !
20590  SUBEND
20600  !
```

B2. INDEX OF SUBPROGRAMMES

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APPENDIX C

MODEL OPERATION: INPUT AND OUTPUT

C1. INPUT DATA

```
410  !                 ***WOOD CHARACTERISTICS***
420  !C,H,O,N,ASH,MC(TO GASIFIER):%; HHV:CAL/G;MC(TO DRYER):%
430  DATA 49.31,4.93,44.73,0.33,0.70,5.35,4716,50
440  !                 ***GASIFIER***
450  !TYPE OF GASIFIER (Seri,Mitsalt,Fluid_bed,Pnl,2cl)
460  DATA "Mitsalt"
470  !                    Ygas(*) FROM GASIFIER, MOLE FRACTION
480  !                    CO,CO2,CH3OH,H2,H2O,CH4,N2,O2
490   DATA 0.2589,0.3511,0.000,0.2920,0.0000,0.0979,0.0000,0.0000
500   !                   FLOW FROM GASIFIER, M/t
510   !                   For normal operation use 1.0
520   DATA 1.00
530   !                   TGAS, 'C
540   DATA 850
550   !                  CHAR_YIELD, FRACTION DRY WOOD FEED, WT BASIS; TSTEAM, 'C
560   DATA 0.0649,208
570   !                   ***REFORMER***
580   !                   T(1):TEMPERATURE OF GAS TO REFORMER
590   DATA 250
600   !                   Tr1,Tr2,'C;Pr(ATM):DATA FOR REFORMER
610   DATA 850,950,20
620   !                    REFORMER STACK O2: FRACTION
630   DATA 0.02
640   !                   METHANE CONC IN OUTLET OF REFORMER
650   DATA 0.01
660   !                   Tm1,Tm2,'C;Pm(kP):DATA FOR METHANOL SYNTHESIS
670   DATA 250,250,5000
680   !                   K1r(STEAM PEFORMING OF CH4)
690   DATA 3929
700   !                   KGAMS(CO TO CH3OH),KGAMS(INVERSE WATER GAS SHIFT::METHANOL
710   !                   KGAMREF (STEAM REFORMING OF CH4)
720   !                   EQUIL COEFFICIENT FORMED FROM ACTIVITY COEFF:FN OF T & P
730   DATA 0.72,0.62,1.00
740  !                  ***CO SHIFT***
750  !                  Tco('C),Pco(ATM),Kgamco
760  DATA 350,20,0.97
770  !                    ***ACID GAS REMOVAL***
780  !                    YFACID(CO2),YFACID(H2O):SPECIFY OUTLET CONDITIONS
790  !                    TACID_GAS, 'C
800  DATA 0.04,0.0,100
810  !                    ***METHANOL***
820  !                    FRSTORE:SPECIFY RECYCLE RATE RELATIVE TO INLET FLOW
```

```
830  !                    If concentration of CH4 in the recycle stream is to be set
840  !                    and recycle rate calculated based on this quantity then
850  !                    make changes indicated in Methanol subprogramme.
860  DATA 1.5
870  !                    ***PRETREAT:DRYER***
880  !                    TDRYER:STACK OUTLET TEMP, °C;STACK_O2:FRACTION
890  DATA 150,0.05
900  !                    ***BOILER***
910  !     TLOWER_STEAM: TEMP STEAM AFTER EXPANDER, °C
920  !     THIGHER_STEAM: TEMP STEAM GENERATED BY BOILER AND FED TO TURBINE, °C
930  !     BOILER_STACK_O2: FRACTION
940  !     TURBINE_EFF: TURBINE EFFICIENCY ,FRACTION
950  DATA 260,400,0.05,0.75
960  !                   ***SPECIFIC HEAT COEFFICIENTS***
970  !CO:
980  DATA 7.0352,-1.46753E-03,3.38378E-06,-1.5668E-09
990  !CO2:
1000 DATA 4.9727,1.6168E-02,-1.10921E-05,2.9243E-09
1010 !CH3OH:
1020 DATA 4.5489,2.1857E-02,-2.9075E-06,-1.92E-09
1030 !H2:
1040 DATA 6.73166,7.6678E-04,-7.9018E-07,5.03619E-10
1050 !H2O:
1060 DATA 7.79678,-1.78036E-04,3.46408E-06,-1.22932E-09
1070 !CH4:
1080 DATA 4.8723,1.07719E-02,5.47676E-06,-3.9375E-09
1090 !N2:
1100 DATA 7.20139,-1.9214E-03,4.1995E-06,-1.65999E-09
1110 !O2:
1120 DATA 6.34224,2.14122E-03,4.62397E-07,-6.00486E-10
1130 !C:GRAPHITE
1140 DATA 2.673,2.617E-03,-1.169E05,0
1150 !            *** HEAT OF FORMATION CAL/M***
1160 !       CO,CO2,CH3OH,H2,H2Og,CH4,N2,O2,H2Ol
1170 DATA -26416,-94052,-48080,0,-57798,-17889,0,0,-68317
1180 !            *** FREE ENERGY OF FORMATION, 25°C:CAL/M***
1190 DATA -32808,-94260,-38620,0,-54635,-12140,0,0,-56690
1200 !                ***CRITICAL CONSTANTS***
1210 !                          **Tc**
1220 DATA 133,304.2,513.2,33.3,647.3,190.7,126.1,154.4
1230 !                          **Pc**
1240 DATA 34.5,72.6,78.7,12.8,217.7,45.9,33.5,49.7
1250 !                    **************
1260 !                ****WOOD COST, $CAN/DRY Kg****
1270 DATA 2.5E-02
1280 !                ***METHANOL FLOW (TARGET): TONNE/D****
1290 DATA 500
1300 !            ***DATA FOR SUPPLY PRICE CALC***
1310 !             ***INTEREST (Discount Factor),FRACTION:YEARS****
1320 DATA 0.07,20
```

C2. OUTPUT: RECYCLE RATIO IN METHANOL UNIT SPECIFIED

```
PRETREATMENT:
  DRYER:
    FEED TO DRYER (DRY WOOD):                     .257M/t    ( 25.484g/t)
    FEED TO GASIFIER (DRY WOOD):                  .224M/t    ( 22.141g/t)
    DRYER PRODUCT COMBUSTED (DRY WOOD):           .034M/t    (  3.343g/t)
    WATER EVAPORATED:      1.336M/t
    MOISTURE CONTENT (WET BASIS, %):
      FEED TO DRYER:  50.000
      DRYER PRODUCT:   5.350
    STACK O2, %:     5.000
GASIFIER:Mitsalt
  FLOWS, M/t:
  DRY WOOD=    .2237  ( 22.14g/t)
  MOISTURE=    .0695
  STEAM=       .0150
  OXYGEN=      .2303
  GAS FROM GASIFIER= 1.2143
  GAS TO PROCESS= 1.0000
  CHAR=        .1197  YIELD=  .0649
  STEAM CONDENSATION FROM GAS= 0.0000
EXTERNAL HEAT SUPPLY, CAL/T=-16079.46
GAS COMPOSITION:
            EX GASIFIER          TO PROCESS
CO:           .2408                .2408
CO2:          .3266                .3266
CH3OH        0.0000               0.0000
H2:           .2716                .2716
H2O:          .0700                .0700
CH4:          .0911                .0911
N2:          0.0000               0.0000
O2:          0.0000               0.0000
 TEMPERATURES: °C
  WOOD AND O2=  25.0
  STEAM=        288.0
  GAS AND CHAR=850.0
 WOOD COMPOSITION, ASH AND N2 FREE BASIS:
  C=49.310  H= 4.930  O=44.730  N=  .330
  ASH=    .700  HHV=4718.000
  SUBC= 4.109  SUBH= 4.930  SUBO= 2.796
  MOL WT= 98.97


 SYNTHESIS GAS:
 CO:           .2408
 CO2:          .3266
 CH3OH:       0.0000
 H2:           .2716
```

```
H2O:         .0700
CH4:         .0911
N2:         0.0000
FLOW, M/t: 1.0000



REFORMER
  TEMP,'C= 850.0000
  PRESS, ATM=  20.0000
  K1 (REFORMING)=3923.0000
  K2 (SHIFT)= 1.1406
  X=  .0760  (K2= 1.1406)
  Y=  .1273  (K1=3928.4168)
                        Ygas        Yirr        Youtr
CO:                   .22419      .21207      .35904
CO2:                  .30418      .28503      .13671
CH3OH:               0.00000     0.00000     0.00000
H2:                   .31426      .28447      .34460
H2O:                  .06311      .12211      .14955
CH4:                  .09426      .08833      .01000
N2:                  0.00000     0.00000     0.00000
FLOW RATE, M/t= 1.10807     1.16360     1.26530
                   STEAM=  .07454

CHECK ELEMENT BALANCE:
                 C        O        H
IN:            .6905   1.0679   1.4043
OUT:           .6905   1.0679   1.4043

EXCHANGER DESIGN
  UA=100.0
          INLET     OUTLET
  HOT:    850.0      388.6
  COLD:   250.0      834.3
COMBUSTION:
  SYNGAS USED FOR FUEL
  STACK O2, %= 2.0
  FLOW, M/t=  .2143

GASIFIER SYNGAS FLOW, M/T= 1.21433591417



CO SHIFT
TEMP ,'C= 350
PRESS, ATM= 20.0
STEAM ADDITION, M/t=   .063
              Yinco   Youtco   Yfco
CO:           .3417    .1801    .1801
```

```
CO2:           .1301     .2037     .2037
CH3OH:        0.0000    0.0000    0.0000
H2:            .3202     .4815     .4815
H2O:           .1907     .0372     .0372
CH4:           .0095     .0095     .0095
N2:           0.0000    0.0000    0.0000
FLOW, M/t:    1.4347    1.4347    1.4347
          BYPASS: 0.0000


ACID GAS REMOVAL
  TEMP:  0.30 °C
              VINACID  YOUTACID
CO:             .1681    .2659
CO2:            .2037    .3400
CH3OH:         0.0000   0.0000
H2:             .4815    .5626
H2O:            .0372   0.0000
CH4:            .0095    .0134
N2:            0.0000   0.0000
FLOWS,M/t:     1.4347   1.0150
BAL RATIO= 2.0940
METHANOL SYNTHESIS
TEMP,°C= 250
PRESS,kPa= 5000
CONVERSIONS:
  OVERALL C (BASED ON CO AND CO2):  .9402
  CO  BASED ON PROC UNIT INLET COMP):  .3984  (Xmetr=  .1151)
TARGET:  RECYCLE RATIO= 1.500
         CH4 CONC (INERT)  .0750
  TARGET USED: RECYCLE
                  YO        Yin       Yout       Yr         Ym
CO:             .2659     .1496     .0500     .0718
CO2:            .3400     .0754     .0827     .0930
CH3OH:         0.0000    0.0000     .1494    0.0000     .3072
H2:             .6605     .6955     .5692     .7054
H2O:           0.0000    0.0000     .0153    0.0000     .0328
CH4:            .0134     .0796     .1034     .1238
N2:            0.0000    0.0000    0.0000    0.0000
FLOW,M/t:      1.0150    2.5375    1.0536    1.5225     .3218
      PURGE:    .1093  (COMP SAME AS RECYCLE)
CHECK FOR EQUIL CONVERGENCE, COMPARE EQUIL CONST
 SPECIFIED:
  K1m=    7.1673  K2m=     .0188
 CALC FROM COMP:
  K1m=    7.1743  K2m=     .0188
CHECK FOR PURGE BALANCE:
               CH4        N2
IN:           .0126    0.0000
```

```
OUT:            .0135     0.0000
CHECK FOR OVERALL ELEMENT BALANCE
                  C          O          H
IN:             .3242      .3511      1.4363
OUT:            .3241      .3513      1.4358


COMPRESSION:
METHANOL UNIT:
                         INLET          RECYCLE
SHAFT POWER, CAL/T: 1111.75          92.99
INLET TEMP, 'C:       100.00         250
OUTLET TEMP, 'C:      243.69         257.27
INLET PRESS, ATM:      20.00          47.32
OUTLET PRESS, ATM:     49.35          49.35


OXYGEN PRODUCTION:
  CRYOGENIC PROCESS
  POWER REQUIREMENTS=   3256.022CAL/t


BOILER
  FEED M/t, DRY BASIS:
    WOOD=  0.000  CHAR=   .120
    MC CHAR, %=  50.000
  STEAM FLOW, M/t=  6.091


STEAM TEMPERATURES, 'C:
  BOILER HIGH TEMP STEAM=  400.000
  TURBINE OUTLET=          200.000
STACK O2, %=  5.000
TURBINE EFF=   .750


OVERALL CONVERSION EFFICIENCY
  C CONVERSION, %= 27.593
  FIRST LAW EFF, %= 41.732


PLANT CAPITAL COSTS, $CAN JAN 1/85
GASIFIER: Mitsalt
BLCC= 3.19240250026E+7
OFFSITE= 1.69850153032E+7
TOTAL PLANT CAPITAL= 1.13745400952E+8


TOTAL OPERATING EXPENSES, $CAN JAN 1/85
WOOD COST, $Kg(DRY)= .025
```

```
MATERIAL AND UTILITY COSTS= 1.38918836539E+7
LABOUR= 5.67595534311E+6
CAPITAL RELATED= 5.40698591417E+6
TOTAL OPERATING= 2.49748249112E+7


SUPPLY PRICE:
YEARS= 20
DISCOUNTING FACTOR, %= 7
SUPPLY PRICE, $/TONNE= 210.055086957
```

C3. CH_4 CONCENTRATION OF RECYCLE STREAM IN METHANOL UNIT SPECIFIED

```
PRETREATMENT:
  DRYER:
    FEED TO DRYER (DRY WOOD):                    .258M/t    ( 25.528g/t)
    FEED TO GASIFIER (DRY WOOD):                 .224M/t    ( 22.180g/t)
    DRYER PRODUCT COMBUSTED (DRY WOOD):          .034M/t    (  3.349g/t)
    WATER EVAPORATED:        1.338M/t
    MOISTURE CONTENT (WET BASIS, %):
      FEED TO DRYER:  50.000
      DRYER PRODUCT:   5.350
    STACK O2, %:      5.000


GASIFIER:Mitsait
  FLOWS, M/t:
  DRY WOOD=    .2241  ( 22.13g/t)
  MOISTURE=    .0597
  STEAM=       .0150
  OXYGEN=      .2307
  GAS FROM GASIFIER= 1.2165
  GAS TO PROCESS= 1.0000
  CHAR=        .1200  YIELD=  .0649
  STEAM CONDENSATION FROM GAS= 0.0000
 EXTERNAL HEAT SUPPLY, CAL/T=-18111.02
 GAS COMPOSITION:
           EX GASIFIER          TO PROCESS
 CO:          .2408                .2408
 CO2:         .3266                .3265
 CH3OH       0.0000               0.0000
 H2:          .2716                .2716
 H2O:         .0700                .0700
 CH4:         .0911                .0911
 N2:         0.0000               0.0000
 O2:         0.0000               0.0000
 TEMPERATURES: °C
   WOOD AND O2=  25.0
  STEAM=        250.0
  GAS AND CHAR=850.0
WOOD COMPOSITION, ASH AND N2 FREE BASIS:
  C=49.310  H= 4.930  O=44.730  N=  .330
  ASH=     .730  HHV=4716.000
  SUBC= 4.109  SUBH= 4.932  SUBO= 2.796
  MOL WT= 30.87


SYNTHESIS GAS:
CO:           .2408
CO2:          .3265
CH3OH:       0.0000
H2:           .2716
H2O:          .0700
CH4:          .0911
N2:          0.0000
FLOW, M/t:   1.0000



REFORMER
  TEMP, C= 850.0000
  PRESS, ATM=  20.0000
  K1 (REFORMING) =3929.0000
  K2 (SHIFT)= 1.1406
  X=  .0539  (K2= 1.1406)
  Y=  .1185  (K1=3925.5453)
                    Ygas        Yinr        Youtr
CO:               .21702      .20010      .34089
CO2:              .29172      .26897      .13198
CH3OH:           0.00000     0.00000     0.00000
H2:               .34460      .31774      .35664
H2O:              .05840      .13181      .15639
CH4:              .08826      .08138      .01412
N2:              0.00000     0.00000     0.00000
FLOW RATE, M/t=  1.19827     1.30068     1.48239
              STEAM=  .10141

CHECK ELEMENT BALANCE:
                 C        O        H
IN:           .7160   1.1314   1.5928
OUT:          .7160   1.1314   1.5928
EXCHANGER DESIGN
  UA=100.0
          INLET     OUTLET
  HOT:    852.0      395.4
  COLD:   250.0      832.6
COMBUSTION:
  SYNGAS USED FOR FUEL
  STACK O2, %= 2.0
  FLOW, M/t=  .2165

GASIFIER SYNGAS FLOW, M/T= 1.21653966874


CO SHIFT
TEMP ,'C= 350
PRESS, ATM= 20.0
STEAM ADDITION, M/t=    .034
               Yinco     Youtco    Yfco
CO:            .3333     .1918     .1918
CO2:           .1291     .2706     .2706
CH3OH:        0.0000    0.0000    0.0000
H2:            .3507     .4922     .4922
H2O:           .1771     .0356     .0356
CH4:           .0093     .0093     .0093
N2:           0.0000    0.0000    0.0000
FLOW, M/t:    1.5161    1.5161    1.5161
          BYPASS: 0.0000


 ACID GAS REMOVAL
   TEMP:  0.00 'C
               YINACID  YOUTACID
CO:            .1918     .2653
CO2:           .2706     .0400
CH3OH:        0.0000    0.0000
H2:            .4922     .6810
H2O:           .0356    0.0000
CH4:           .0099     .0137
N2:           0.0000    0.0000
FLOW,M/t:     1.5161    1.0958
BAL RATIO= 0.9995


 METHANOL SYNTHESIS
 TEMP,'C= 250
 PRESS, kPa= 5000
 CONVERSIONS:
   OVERALL C (BASED ON CO AND CO2):  .3719
   CO (BASED ON PROC UNIT INLET COMP):  .4709  (=meth= .1240)
 TARGET:  RECYCLE RATIO= 1.500
          CH4 CONC (INERT)  .0750
   TARGET USED: INERT
                YO         Yin         Yout        Yr          Ym
 CO:           .2653      .1922       .0765       .0977
 CO2:          .0400      .0781       .0943       .1170
```

```
CH3OH:     0.0000   0.0000    .1837   0.0000     .9215
H2:         .6810    .5959    .5713    .7111
H2O:       0.0000   0.0000    .0129   0.0000     .0085
CH4:        .0157    .0426    .0597    .0743
N2:        0.0000   0.0000   0.0000   0.0000
FLOW,M/t:  1.0958   2.1709   1.5976   1.0755     .3121
      PURGE:     .1993  (COMP SAME AS RECYCLE)
CHECK FOR EQUIL CONVERGENCE, COMPARE EQUIL CONST
 SPECIFIED:
  K1m=    7.1673  K2m=      .0188
 CALC FROM COMP:
  K1m=    7.1737  K2m=      .0188
CHECK FOR PURGE BALANCE:
              CH4        N2
IN:          .0150    0.0000
OUT:         .0149    0.0000
CHECK FOR OVERALL ELEMENT BALANCE
              C           O          H
IN:          .3496      .3784     1.5524
OUT:         .3494      .3784     1.5513


COMPRESSION:
METHANOL UNIT:
                        INLET        RECYCLE
SHAFT POWER, CAL/T: 1200.20          65.70
INLET TEMP, 'C:       100.00        250
OUTLET TEMP, 'C:      243.67        257.41
INLET PRESS, ATM:      20.00         47.32
OUTLET PRESS, ATM:     49.35         49.35


OXYGEN PRODUCTION:
  CRYOGENIC PROCESS
  POWER REQUIREMENTS=   3261.763CAL/t
BOILER
  FEED M/t, DRY BASIS:
    WOOD=  3.000  CHAR=   .120
    MC CHAR, %=  50.000
  STEAM FLOW, M/t=  6.193
  STEAM TEMPERATURES, 'C:
    BOILER HIGH TEMP STEAM=  400.000
    TURBINE OUTLET=          286.000
  STACK O2, %=  5.000
  TURBINE EFF=   .750


OVERALL CONVERSION EFFICIENCY
  C CONVERSION, %= 27.517
  FIRST LAW EFF, %= 41.617
```

```
PLANT CAPITAL COSTS, $CAN JAN 1/85
GASIFIER: Mitsalt
PLCC= 9.19773451877E+7
OFFSITE= 1.70328715766E+7
TOTAL PLANT CAPITAL= 1.13861749279E+8


TOTAL OPERATING EXPENSES, $CAN JAN 1/85
WOOD COST, $Kg(DRY)= .025
MATERIAL AND UTILITY COSTS= 1.39304040007E+7
LABOUR= 5.69169425733E+5
CAPITAL RELATED= 5.41050478239E+6
TOTAL OPERATING= 2.5032603641E+7


SUPPLY PRICE:
YEARS= 20
DISCOUNTING FACTOR, %= 7
SUPPLY PRICE, $/TONNE= 210.463343218
```